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PAPERS READ BEFORE THE CHEMICAL SOCIETY.

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PAPERS READ BEFORE THE CHEMICAL SOCIETY.

I.—*Modifications of Double Sulphates.*

By SPENCER UMFREVILLE PICKERING, M.A. Oxon, Professor of Chemistry at Bedford College.

IN a previous communication to this Society (*Chem. Soc. J.*, Trans., 1884, 686), attention was drawn to the great discrepancies which exist in the determinations of the heat of dissolution of anhydrous potassium magnesium sulphate, it being, according to Thomsen, 10,602 cal., and according to Graham only 7000 cal. An investigation of the corresponding copper salt, $CuK_2(SO_4)_2$, led to an explanation of these discrepancies.

Potassium Copper Sulphate.

This salt may be prepared without any difficulty by mixing hot concentrated solutions of the constituent sulphates in equivalent proportions, and allowing the mixture to cool. The liquid should not be heated to within 20° or 30° of its boiling point, otherwise an abundant crystalline precipitate will be formed, which, according to Brunner (*Pogg. Ann.*, **15**, 476), consists of a basic double salt having the composition $CuK_2(SO_4)_2,2CuSO_4,CuO,4H_2O$, decomposable by water, leaving an insoluble residue of the tetrabasic copper sulphate,

$$CuSO_4,3CuO.$$

A considerable quantity of the crystallised salt, $CuK_2(SO_4)_2,6H_2O$, having been prepared in the above manner, the crystals were powdered, washed, and dried by exposure to air, after which they

were found to contain the theoretical percentage of water within experimental error.

When heated at 100°, this hydrated salt parted quickly with the whole of its water, leaving the anhydrous salt in the form of a blue powder as dark in colour as the hydrated substance itself: when, however, this blue salt was heated to a temperature of 150—200°, it was found to lose its colour and become white, or very nearly white; this white modification in its turn underwent a change when the temperature was further raised to about 300° or 400°, and became again blue or bluish-green. This third modification remained apparently unchanged by any additional increment of temperature till the melting point of the salt was reached at a low red heat. The molten salt forms an opaque green liquid, which solidifies to form a glassy mass; as soon, however, as the temperature falls sufficiently low, this glass suddenly crumbles into an opaque blue powder resembling in every respect the blue modification obtained at 400°. The behaviour of the fused salt has been noticed by previous observers (Thomsen, *J. pr. Chem.*, **18**, 35), but the white modification has hitherto escaped observation; indeed, when operating on small quantities of the salt, it appears difficult to obtain it at all.

It is necessary to cool the fused or strongly heated salt as quickly as possible, for, if cooled slowly, it will often revert partially to the white form, and it is, moreover, necessary to fuse it in quantities not exceeding 5 or 6 grams, in order to avoid any decomposition, as it begins to evolve sulphuric anhydride at a temperature very little above its fusing point.

The curious changes of colour experienced by this salt suggested its existence in distinct modifications, which might be more fully investigated by measuring their heats of dissolution.

Various specimens were, therefore, prepared and examined in this way. The results thus obtained are embodied in Table I (p. 6).

The first column in this table gives the number by which the samples were designated for the convenience of future reference. Nos. 3415, 3424, and 3425 were obtained from a totally different preparation of the hydrated salt to that from which the others were obtained.

w = weight of salt taken.

W = the water equivalent of the calorimeter and its contents, the volume of the water in it being 601,678 + 0·016 T° c.c., which, according to Berthelot's simplified method of calculation, is reckoned as being equivalent to the same number of grams with a specific heat of unity (see *Mécanique Chimique*, **1**, 190).

Column VII records which thermometer was employed in the

experiment; the temperature τ, t, and t' being given in the arbitrary degrees of these instruments.

τ = temperature of the salt at the moment of its introduction into the calorimeter. t = the initial, and t' the final temperature of the calorimetric liquid, corrected for (1) the temperature of the salt according to the equation $\frac{(t - \tau)wc}{W + w}$, where c is the specific heat of the salt; (2) the exposure of the mercurial column to the temperature of the air; (3) the calibration correction.

The molecular heat of dissolution (Column XII) is given by the equation $M = \frac{(t' - t)\alpha WM}{w}$, where M is the molecular weight of the salt (333·02), and α the mean value of the arbitrary degrees of the thermometers in degrees centigrade, this being in the case of thermometer 81, 0·38663°, and with 83, 0·38046°.

The next column gives the initial temperature in degrees centigrade.

The figures in the other columns will be explained shortly.

The proportion of water to salt taken was about 800 : 1 mol.

For experimental error, &c., see Trans., 1884, 686.

Some small correction should be applied to some of the numbers given in this table, owing to the presence of a little basic and insoluble salt which the white specimens always contained. The greatest quantity which was ever found amounted to 0·2 per cent. (in the case of the white modification), and would necessitate a correction of about + 12 cal.; some of the specimens of the third modification contained a similar impurity also, not exceeding, however, 0·06 per cent., corresponding to 6 cal.; these amounts are so small in comparison with the experimental errors that it was not thought necessary to correct for them. The first modifications as well as the fused specimens contained no such impurity.

The majority of the experiments quoted in this table were performed at an initial temperature of 18·25° C., and, confining our attention for the moment to these experiments only, it will be seen that all the blue specimens which were obtained at low temperatures dissolved with practically the same evolution of heat, namely, 9709 cal.; the white specimens evolve a very much smaller amount of heat on dissolving, about 6200 cal. only, though the various numbers here are not so closely concordant as they are with the blue specimens, from a cause which will be mentioned shortly; lastly, the blue specimens obtained at higher temperatures evolve an amount of heat differing from either of the others, namely, 8407 cal. There can be no doubt, therefore, that the successive changes of colour indi-

cate the formation of distinct modifications of the salt, which may be conveniently designated as α, β, γ.

The method of preparation of the different specimens was varied as much as possible. No difference is made in the nature of the α-modification, whether it is obtained at the lowest temperature at which dehydration is complete, or at the highest temperature (about 130° as indicated by a thermometer in an air-bath*) which can be employed without risking the formation of some of the white salt. The various white specimens were obtained either direct from the hydrated salt, or from the blue anhydrous modification, and at temperatures ranging from 180° to 220°, but in all cases they yielded identical numbers, showing that this modification also has a perfectly definite existence. The second blue or γ-modification, which begins to appear at 250—300°, is in a similar manner perfectly stable throughout a considerable range of temperature, and even after fusion yields the same numbers on dissolution. The specimen, No. 2737, which alone gave numbers lower than the others, was known to contain some of the white modication unaltered.

The heat of dissolution decreases, of course, and decreases rapidly, with the temperature of the water, and we can examine those results obtained with the β- and γ-modifications at temperatures other than 18·25°, only by comparing them with the heat of dissolution of the α-modification at identical temperatures. Where M_α and M_β represent the heats of dissolution of the α- and β-modifications respectively at T°, the heat of formation of the β- from the α-modification at that temperature is $M_\alpha - M_\beta$. The values of M_α at the necessary temperatures are given in Column XIV, having been deduced from numerous experiments, the details of which it is not necessary to give here, and the values of $(M_\alpha - M_\beta)$ and $(M_\alpha - M_\gamma)$ are given in Column XV. These values, the heat of transformation of the α- into the β- and γ-modifications will, however, not be constant quantities, unless the specific heats of all the modifications are identical. Where this is not the case, the heat evolved, Q', in any chemical reaction at T', may be calculated from that evolved, Q, at any other temperature T by means of the equation $Q - c'(T - T') = Q' - c(T - T')$, in which c represents the sum of the specific heats of the reacting substances, and c' that of the substances formed (see Berthelot, *Méc. Chim.*, 1, 105). It was necessary, therefore, to determine the specific heats of the salts in question; the details of these determinations will be more conveniently given elsewhere, the general results only being here

* In such a case, the thermometer being placed above a dish containing some 100 grams of the salt, the lower portions of the salt get heated, no doubt, 20° or 30° above the thermometric reading.

stated. The molecular heats of the three modifications were found to be—

$$c_\alpha = 56{\cdot}025$$
$$c_\beta = 51{\cdot}24$$
$$c_\gamma = 58{\cdot}735$$

Substituting these values for c and c' in the above equation, the results obtained at the various temperatures were all reduced to 18·25°, and entered in Column XVI of the table.

In the first place with regard to the γ-modification, the numbers thus obtained are not identical, as they should be, but show a regular increase with the temperature; it is difficult to account for this fact otherwise than by assuming that the specific heat of this modification is considerably greater at these temperatures (8—23°) than experiment showed it to be at 8—43°. In order to render the figures in the last column identical, the value of c_γ would have to be 70 instead of 58·7, or at any rate the difference between the two specific heats c_α and c_γ would have to be five or six times greater than the determinations gave it. Such a supposition is scarcely admissible, and it will be preferable to take those experiments only which were performed at 18·25°, and which give + 1302 cal. as the heat value of the transformation of the α- into the γ-modification at that temperature.

The numbers in the last column, which refer to the formation of the white modification, show also a considerable variation, but here the variation may be accounted for without difficulty.

Berthelot has shown (*Ann. Chim. Phys.* [5], 29, 295, *et seq.*) that most double as well as single salts after fusion do not at once attain their normal and stable condition as regards their thermal properties, and it seems not improbable that a similar period of instability may intervene after they have been heated, even without fusion (see Trans., 1885, 99), especially if, as in the present case, this heating has been accompanied by some distinct molecular rearrangement. Unfortunately, at the time when these experiments were made, now nearly two years ago, Berthelot's results had not been published, and the intervals which had elapsed between the preparation and dissolution of a sample were not accurately noted; the dates which are given in Column IV are, therefore, for the most part approximations only; but, nevertheless, they show satisfactorily that the white samples dissolve with an evolution of about 230 cal. more after they have been kept for some days than they do when freshly prepared.

Taking the different samples separately—

No. 2739 dissolved after three days with a heat evolution which gives the value of $M_\alpha - M_\beta$ to be 3590 cal. (Expt. 9); after 10 days the value (calculated for 18·25°) was reduced to

3326 (Expts. 16 and 17) and 3296 (Expts. 7 and 8); after 130 days, to 3396 (Expt. 14) and 3393 (Expt. 15): an average reduction of $\left(\frac{264 + 294 + 194 + 197}{4} =\right)$ 237 cal.

No. 2750 after three days gave the value 3476 (Expt. 12); after 10 days, 3299 (Expts. 18 and 19); and after 130 days, 3284 (Expt. 13), showing an average reduction of $\left(\frac{177 + 192}{2} =\right)$ 185 cal. in this value.

No. 3425 dissolved after one day gave 3602 (Expt. 20); and after 60 days, only 3271 (Expts. 21 and 22): a reduction of 331 cal.

No. 2716 dissolved after one day gave 3528, *i.e.*, 200 cal. above the average of other samples dissolved after keeping.

No. 3415 alone showed no change on being kept 44 days; but as it gave only 3360 cal. as the value of the reaction when dissolved immediately after preparation, it would appear as if some peculiarity in the details of its treatment had reduced it at once to that state in which this modification remains stable.

Summing up these results, it seems evident that some change takes place which is complete in about 10 days, and which results in the salt dissolving with an evolution of about 230 cal. more than it does when freshly prepared, the actual numbers being 6159 cal. at first, and 6489 cal. eventually, the transformation of the α- into the β-modification evolving 3550 and 3220 cal., according as either the former or the latter of these above numbers is taken; preference should be, perhaps, given to the latter, as it corresponds to the more stable condition. This number will therefore be adopted.

A comparison of Expt. 6 with Expts. 1 to 5 shows that the α-modification undergoes no change of this description; and a comparison of Expt. 27 with 28, and of 34 with 31 to 33, shows the same fact with regard to the γ-modification. Expt. 15 proves that prolonged heating of a white specimen, at temperatures below that of its preparation, does not induce any change in it.

The heat development on the passage of one modification into another, as given above, is calculated, of course, on the assumption that all the three modifications, when dissolved in water, form identical solutions, an assumption which the appearance and behaviour of the solutions, as well as the absence of further thermic effects, fully justifies.

The heat of formation of the double salt from its constituent sulphates, x, will be given by the following equation:—

$$N = x + M_{KMg} - (M_K + M_{Cu}),$$

in which M_{KMg}, M_K, and M_{Cu} are the molecular heats of dissolution of the double salt of potassium sulphate, and of copper sulphate respectively,* and N the heat disturbance on mixing solutions of the single sulphates. This latter quantity was found to be *nil*, in accordance with the observations of other physicists, and the values of M_K and M_{Cu} were found by means of numerous experiments to be $-$ 6495 and 15633 respectively at 18·25°; the algebraic sum of these is + 9138, and hence the heat of formation of the α double salt will be (9138 $-$ 9709 =) $-$ 571 cal., *i.e.*, it is an *endothermic* compound. The other two modifications on the contrary would be formed by *exothermic* reactions:—

$$[K_2SO_4 + CuSO_4 = \beta\text{-}CuK_2(SO_4)_2] = 2649 \text{ cal.},$$
$$\text{and } [K_2SO_4 + CuSO_4 = \gamma\text{-}CuK_2(SO_4)_2] = 731 \text{ ,,}$$

That all these three salts are in reality compounds, and not mere mixtures of the uncombined sulphates of copper and potassium, is clearly shown by the fact that none of them dissolves with the heat evolution with which the mixed salts would, namely 9138 cal., and that those two modifications which approach most nearly to this quantity are both blue substances, whereas a mixture would be white; the only modification which is white dissolves with an evolution of as much as 2649 cal. less than a simple mixture would do.

It remains only to be added that whereas the first change undergone by this salt, the passage of the α- into the β-modification, is an exothermic action evolving 3220 cal., the second change, that of the β- into the γ-modification, is an endothermic action, absorbing 1918 cal., as measured at 18·25°.

The mean of two determinations of the heat of dissolution of this salt which were made by Thomsen gave 9396 cal. at 17·27°, whereas at this temperature the α-modification, according to my experiments, would evolve 9617 cal. on dissolving, indicating that Thomsen's specimen had been overheated, and contained some of the β-modification. The experiments, however, are not strictly comparable with mine, as he used a proportion of water amounting to only two-thirds of that used by myself.

Potassium Magnesium Sulphate.

An investigation of potassium magnesium sulphate conducted on the same lines as that of its copper analogue was found to be complicated by various circumstances.

* If the single sulphates are dissolved in 400 molecules of water, the double sulphate must be dissolved in 800 molecules in order to make this equation correct. These proportions were taken.

In the first place, considerable difficulty was met with in preparing the salt itself in a state of purity. The double salt is considerably more soluble than its component sulphates, and, therefore, unlike the copper salt, it does not crystallise out on mixing saturated solutions of the two sulphates. The mixed liquids should be evaporated while hot, and then allowed to cool; spontaneous evaporation should not be resorted to, and the magnesium sulphate should be present in considerable excess, otherwise the crystals separating out will contain a large quantity, or even consist entirely of uncombined potassium sulphate. Moreover, since the double salt is entirely decomposed by an excess of water, the crystals should be washed free from mother-liquor only by means of a saturated solution of the double salt itself. After many unsuccessful attempts, a large quantity of the crystallised salt was prepared containing the theoretical percentage of water; from this, the anhydrous specimens were obtained. But here another difficulty arose. Just like magnesium sulphate itself, the double salt does not lose its water at the same low temperature, and with the same ease as the copper compound does. The whole of its water is not evolved below 155°, and, as it was feared that this temperature would be sufficiently high to induce some change in the constitution of the salt, the same expedient was adopted as in the case of magnesium sulphate (Trans., 1885, 101), namely, dehydrating the salt as far as possible at the required temperature, and making a correction for any residual water which is still retained. This correction was made in the same way as for magnesium sulphate, necessitating a knowledge of the heat of dissolution of the hydrated salt as well as that of the anhydrous salt at some particular temperature. The former of these quantities was found to be $-$ 9777, and the latter, as will be shown below, + 12037 at 22·28°, and, consequently, the correction to be applied to the numbers obtained with a sample retaining, for instance, 0·6 per cent. of the total water present when fully hydrated would be $\frac{0 \cdot 6}{100}$ of (12037 + 9777) cal. The various corrections are given in Column X of Table II (p. 9), while the method of preparation and other details are given in the last column. All the experiments in this case were made at the same temperature, 22·28° C., with the exception of those with sample No. 3432, where the results at a higher and a lower temperature gave the means of calculating what the number would have been obtained at 22·28°. The symbols used are identical with those in Table I. The sp. ht. of the salt was taken as 0·17.

To begin with, we are met by the same fact observed in the case of the copper salt; that all the specimens prepared at low temperatures, ranging in this case from 110° to 155°, are identical in nature, and give

TABLE II.—*Heat of Dissolution of Anhydrous Potassium Magnesium Sulphate*, $MgK_2(SO_4)_2 = 293·64$.

$\frac{3}{80}$ mol. = 11·013 grams.

I. Sample.	II. w.	III. W.	IV. Therm.	V. τ.	VI. t.	VII. t'.	VIII. $t'-t$.	IX. M.		X. Correction.	XI. M corrected.			XII. Remarks.
1. 3054	11·067	614·27	81	28·68	32·117	33·9495	1·8325	11559	11603	+ 417	12020		12037	Prepared at 110° C.; retained 1·92 per cent. of the total water.
2. 3054	11·094	614·27	81	28·86	32·1875	34·0385	1·851	11648						
3. 2796	11·184	614·27	81	36·36	32·324	34·234	1·910		11925	+ 120	12045	12055		Prepared at 130°; retained 0·60 per cent. water.
4. 3000	11·049	614·27	81	35·06	32·0625	33·9515	1·889		11925	+ 54	11989			Prepared at 130°; retained 0·25 per cent. water.
5. 2796 & 3000	11·011	614·27	81	32·77	32·230	34·134	1·904		12071	+ 87	12159			
6. 3039	11·140	614·27	81	31·53	32·2315	34·163	1·9215	—	—	0	12104	12027		Prepared at 155°; anhydrous.
7. 3039	11·027	614·27	81	32·19	32·2285	34·116	1·8875	—	—	0	11949			
8. 3432	11·240	614·30	81	36·72	37·1605	39·008	1·8475	11475 at 24·22° C.		giving at	22·28°		11112	Prepared at 170°.
9. 3432	11·139	615·97	81	28·84	28·859	30·590	1·731	10878 at 21·01° C.						
10. 2794	11·037	614·27	81	30·19	32·222	33·938	1·716	—	—	—	10845		10936	,, 192°.
11. 2794	11·070	614·27	81	28·08	32·027	33·772	1·745	—	—	—	11010			
12. 2793	11·138	614·27	81	30·36	32·162	33·630	1·468	—	—	—			9201	,, 215°.
13. 3038	11·171	614·27	81	31·96	32·221	33·5715	1·3505	—	—	—			8440	,, 240°.
14. 3003	11·118	614·27	81	32·76	32·276	33·542	1·266	—	—	—			7949	Prepared below a red heat.
15. 3001	11·090	614·27	81	31·17	32·123	33·352	1·229	—	—	—			7736	,, at a red heat.
16. 3002	11·170	614·27	81	31·28	32·200	33·403	1·203	—	—	—			7518	Partially fused.
17. 3040	10·931	614·27	81	32·31	32·1455	33·309	1·1635	—	—	—			7431	Fused.
18. 3050	11·011	614·27	81	32·21	32·206	33·4715	1·2655	—	—	—			8023	Fused. Dissolved 4 days afterwards.
19. 3070	11·014	614·27	81	34·23	32·258	33·438	1·180	—	—	—	7207		7388	Fused. Dissolved 2 hours afterwards.
20. 3070	10·946	614·32	80	32·93	31·444	32·601	1·157	—	—	—	7570			Fused. Dissolved 1 year afterwards.

the same evolution of heat on being dissolved, namely 12037 cal. at 22·28°, the numbers obtained being very concordant, when it is remembered that a correction depending on the accurate determination of a very small quantity of water had to be applied to most of them. 155° appears, however, to be very near the limit within which such results are obtained; when heated to 170° the samples show a considerable decrease in their heats of dissolution, just as in the case of the copper salt, and this decrease becomes rapidly greater as the temperature employed is higher, till it reaches a climax in the fused specimens, of which the heat of dissolution is only about 7400 cal., or not much more than one half of that of the specimens prepared below 155°, and which may be termed the α-modification.

No modification intermediate between the α-modification and the fused salt appears here, as is the case with the copper salt, but it would, I think, be rash to say that such does not exist. It is a characteristic of the magnesium salts, in contradistinction to the copper salts, that their dehydration, and the various changes which they undergo, not only take place at higher temperatures, but are merged one into another, so that it is often difficult to obtain one of the products free from a certain amount of the others (see Trans., 1885, 101). Such is very probably the case with the double salt. It may be either that an intermediate modification is formed between 155° and a red heat, but that the range of temperature throughout which it is obtainable is so small that the conditions of the present experiments never sufficed to produce it unmixed with the other two modifications (in which case the fused salt should be termed the third or γ-modification), or else it may be that the temperature at which the changes take place being so much higher than they are in the case of the copper salt, the very highest temperature (a bright red heat) which the salt is capable of bearing without decomposition is high enough to form only the second instead of the third modification; if this be so, the fused salt should be termed the β-modification. The latter view is, perhaps, preferable, seeing that the heat of dissolution of this last modification is so much smaller than that of the first one, bearing towards it about the same ratio as the β- does to the α-potassium copper sulphate.

The fused salt exhibits two peculiarities which the unfused samples do not. When thrown into water, it dissolves with extreme slowness, it does not cake, but forms a milky liquid which becomes clear only after the lapse of about 25 or 30 minutes. This has also been noticed by Berthelot (*Ann. Chim. Phys.* [5], **29**, 329), and resembles, though in an intensified form, the behaviour of monohydrated magnesium sulphate. The second peculiarity is that when first put into water, a fall of nearly 0·1° precedes the rise in temperature: this, no doubt,

is due to its passage into the α-modification previous to its dissolution.

The length of time required for the dissolution of the fused specimens renders the heat determinations very difficult; indeed, these can be regarded as approximations only. Omitting Expt. 18, which appears to be exceptionally high, the mean of the last five experiments gives 7431 cal. as the heat of dissolution of β-$MgK_2(SO_4)_2$, and the value of the transformation of the α- into the β-modification as + 4606 cal., measured at 22·28°.

According to my own experiments, potassium sulphate dissolves in 400 mols. of water, at this temperature, with an absorption of 6200 cal., and magnesium sulphate, under like conditions, with an evolution of 20722 cal. This gives the following values for the heat of formation of the double salt from its component sulphates:—

$$[MgSO_4 + K_2SO_4 = \alpha\text{-}MgK_2(SO_4)_2] = 2485,$$
$$[MgSO_2 + K_2SO_4 = \beta\text{-}MgK_2(SO_4)_2] = 7091,$$

both reactions being exothermic.

Berthelot (*loc. cit.*) determined the heat of dissolution of a specimen of the fused salt; his results when reduced to 22·28° become—

(1)	Dissolved at once	....	8039 cal.
(2)	„	after 3 weeks	7132 „
(3)			6432 „
(4)	„	and finely powdered	5588 „*

from which he concludes that after being kept, this salt dissolves with a decreased evolution of heat, due to its parting with some of the heat it had absorbed during fusion, and further, that powdering facilitates this loss. My own experiments, on the contrary, if they show any change at all in the behaviour of the salt when kept, show an *increase* in the heat of dissolution (comp. Expt. 18 with 17, and 20 with 19), a change similar in nature to that which certainly takes place with the β-copper salt.† The difficulties of experimenting in this case, however, are so great that much weight cannot be attached to these

* Berthelot's actual numbers are—(1) at 17°, 7300 cal.; (2) and (3) at 20·1°, 6880 and 6180 cal.; (4) at 20·8°, 5421 cal. Taking with these my own determinations of the heat of dissolution of potassium sulphate and of magnesium sulphate at these three temperatures—which are with the former −6600, −6340, and −6300, and with the latter 20383, 20610, and 20654 cal. respectively—we get for the value of the equation $[MgSO_4 + K_2SO_4 = \beta\text{-}MgK_2(SO_4)_2]$ 6483, 7390, 6432, and 5588 cal. in the four experiments, and the difference between these quantities and the sum of the heats of dissolution of magnesium and of potassium sulphate at 22·28° produces the numbers given in the text.

† Neither the fused copper nor any specimens of the γ-modification showed any change on keeping.

differences, and it will be sufficient to remark that, on the whole, Berthelot's experiments are fairly concordant with my own, the mean of his giving 6798, or that of his first three 7201 cal.* against the mean which I have taken for mine, 7431 cal.

The salt examined by Thomsen (*J. pr. Chem.*, 18, 27), dissolved with an evolution of 900 cal. less than that of the α-modification, showing that this preparation was either not anhydrous or that it had been over-heated and partially converted into the β-modification.

The great insolubility of anhydrous alum points, I think, to the probability of its being in reality different in constitution from the hydrated salt; unfortunately this very insolubility and the difficulty with which it parts with its water renders any experiments similar to the present ones impossible. It appears to be a moot point whether anhydrous alum is absolutely insoluble or not; so far as my experience goes it is certainly not, but at the same time I have found it quite impossible to deprive alum entirely of its water without causing it to lose a very appreciable amount of sulphur trioxide. Pure anhydrous alum is probably unknown.

II.—*Modifications of Double Sulphates.*† Part II. *Specific Heat Determinations.*

By Spencer Umfreville Pickering, M.A. Oxon., Professor of Chemistry at Bedford College.

Double sulphates of the type $M''M'(SO_4)_2,6H_2O$ were originally regarded by Graham (*Phil. Mag.*, 6, 327, 417; 10, 216, &c.) as derived from the corresponding heptahydrated magnesian sulphates by the displacement of one of the molecules of water contained in them by one molecule of an alkali-metal sulphate. Thomsen (*J. pr. Chem.*, 18, 29) controverted this idea by attempting to prove that the

* All the specimens used by me were finely powdered, but the powdering was performed as soon as the fused salt had solidified and while it was still quite hot. It is possible that a slight absorption of moisture during the powdering of Berthelot's specimen, *while cold*, may be the cause of low results of Expt. 4. The proportion of water used by Berthelot was smaller than that used in my own experiments, and hence an absolute concordance of results cannot be expected.

† This communication formed part of a paper entitled "Notes on the Constitution of Hydrated and Double Salts," which was read before the Society. The theoretical portion of this paper will be published hereafter.

heat of combination of the various water molecules in the double sulphate was very different from that of the water molecules in the corresponding single sulphate. I have already shown, however (Trans., 1885, 102), that the experimental data on which Thomsen relied were incorrect, and I shall elsewhere endeavour to prove that his argument was founded on a theory which is quite inadmissible.

Substitution or displacement is one of the many ideas in chemistry which do not admit of any exact definition, and we can only settle whether one substance is a true substitution-product of another by general considerations as to the mode of its formation, and the extent to which it retains the fundamental characteristics of the parent substance.

The case now under consideration is, I think, as true an instance of substitution as any which can be adduced. The manner in which the double sulphates are obtained is of the simplest character, and they exhibit the peculiarities of the sulphates from which they are obtained, even to the most minute details.

The heptahydrated sulphates lose $6H_2O$ at about 100°, leaving the monohydrate $M''SO_4,H_2O$, whilst at the same temperature the double salts part with their $6H_2O$, leaving the salt $M''SO_4,K_2SO_4$. In the case of the copper compounds, both of these are of a light blue colour, and both, when raised to nearly 200°, are decomposed, forming white substances, the anhydrous salt in the one case, and some differently constituted double salt in the other. The peculiarities which distinguish magnesium sulphate from copper sulphate are accurately reproduced in the double salts which it forms; the monohydrate is not obtainable at 100°, but requires a temperature of 150—160° for its formation, and begins to suffer decomposition at a few degrees higher; in like manner the double salt does not part with its water below 155°, and begins to pass into another modification at 170°; the monohydrate cannot be completely decomposed at a temperature below 250—300° instead of 200°, as in the case of the copper salt, and the double salt also requires a temperature considerably higher than 200° to change it into the second modification.

Person was the first to show that the specific heat of a hydrated salt is equal to the sum of the specific heats of the anhydrous salt and of the water contained in it, reckoned as *solid* water. Subsequent experiments have invariably confirmed this view, and, though I have reason to doubt its absolute correctness, it is probable that no direct determination of specific heats would be sufficiently accurate to detect any flaw in it. Now, if it were found that the specific heats of the double sulphates resembled those of the hydrated sulphates in being equal to the sum of those of their constituents, such a fact would lend strong support to the view that they were similar in constitution to these

hydrated salts. An investigation of the specific heats of the three modifications of anhydrous potassium copper sulphate was, therefore, undertaken.

The method employed in these determinations consisted in dissolving a portion of the salt in water under precisely the same conditions as for the determination of the heat of dissolution, except that the temperature of the salt, instead of being nearly identical with that of the calorimetric water, was about 35° higher. The salt to be dissolved was weighed out into a short wide test-tube fitted with a small thermometer; this tube was fixed in a short-necked flask nearly full of water, the whole being heated in an air-bath to the required temperature. The flask with the water acted as a jacket to the tube containing the salt, thus allowing its removal from the bath to the calorimeter without any appreciable alteration in temperature during the few seconds so occupied. This method cannot of course claim any of the accuracy attained by Pape, Kopp, and others using very elaborate apparatus, but it was found to give results sufficiently accurate for the present purposes.

The specific heats of salts as given by different authorities differ so much that it was thought advisable to make determinations of those of copper and of potassium sulphate, at the same time, and with the same apparatus as the double salts. The results are given in the accompanying table (p. 16), where the symbols used are similar to those in the tables in the previous communication. In each case the *same* sample was used both for the determination of the specific heat and of the molecular heat of dissolution, M.*m* is the molecular heat of dissolution in the specific heat experiments without any correction for the salt temperature τ, which, in these cases, is given in degrees centigrade, as also is the interval through which the salt was cooled $(\tau - t)$. The other temperatures are given in arbitrary degrees as previously. c is the specific heat, water $= 1$; and c_m the molecular specific heat.

The three modifications of potassium copper sulphate, it will be seen, are as clearly distinguished by their different specific heats as they are by their different heats of dissolution. The α gives 56·025, or 0·168, the β 51·24, or 0·154, and the γ 58·735, or 0·176. Now the sum of the specific heats of copper sulphate and potassium sulphate is 54·46, or 0·164, but it is probable that this is somewhat smaller than it should be, for, owing to the powdery nature of anhydrous copper sulphate, some particles of it often float on the calorimetric water before they sink, and these must consequently part with some of their heat to the air, thus giving too small a value for the specific heat of the salt: were it not for this, the sum of the specific heats of the mixed sulphates would no doubt approach more nearly to that of the

α-modification of the double salt than it does. Even as it is, however, the numbers are sufficiently concordant* to show that if any of the modifications has a specific heat nearly corresponding to that of a mixture, it is the α-, and not the β- or γ-modification. It is in the α, therefore, if in any, that the potassium sulphate present appears to perform the same function as water in the hydrated single salt. Such a view is in full accordance with the fact that the α-modification is obtained from the crystallised salt at the lowest possible temperature, and that this latter in its mode of formation and general characteristics closely resembles the fully hydrated single sulphate.

It will be noticed that the heat of combination of $MgSO_4 + K_2SO_4 = 2485$ cal., whereas $MgSO_4 + H_2O = 7016$ cal.; and again, that $CuSO_4 + K_2SO_4 = -571$ cal., whereas $CuSO_4 + H_2O = 5143$ cal.; the molecule of water which is combined with considerable energy being displaced by a molecule of potassium sulphate which combines with but feeble energy. It must be remembered, however, that it is the *hydrated*, and not the *anhydrous* salt which is prepared from the mixed sulphates, and when we take the heat-formation of this we find that in the case of the copper salt, whereas the sulphates K_2SO_4 and $CuSO_4 5H_2O$ in crystallising out separately would evolve 9212 cal., the double salt would evolve 13,728 cal., and hence the facility with which it may be formed, and its perfect stability when formed; the magnesium salt, however, cannot be formed with the same ease, and is entirely decomposed by excess of water;† this is due to the fact that in crystallising out it would evolve only 9851 cal., a quantity smaller than that which $MgSO_4, 7H_2O$, and K_2SO_4 would separately, 10,310 cal. Its formation is possible only in the presence of a large excess of magnesium sulphate, or else at a high temperature, where the relative values of some of these quantities are no doubt changed.

The absence of any thermal disturbance on mixing solutions of the component sulphates is generally taken as indicative of the non-existence of the double salts in solution. In the case of the potassium magnesium sulphate this may be so, for this salt is entirely decomposed by water, but it can scarcely be so with the copper salt, for, if it were, it would be difficult to see why any of it should separate out at all on mixing the solutions, unless it be regarded as an insoluble

* Quite as concordant as they are found to be with hydrated salts.

† A sample of $CuSO_4, K_2SO_4, 6H_2O$, which gave on analysis 24·48 per cent. of water (theory 24·448) after being washed continuously till three quarters of it had been dissolved, contained 24·456 per cent., *i.e.*, the same as before the washing. A sample of the magnesium salt containing 26·809 per cent. of water (theory 26·822), after being similarly treated was found to contain only 18·89 per cent., showing that it contained 30 per cent. of uncombined potassium sulphate.

substance, a view which is hardly reconcileable with its composition and properties.*

By means of the specific heats, the heat of formation of the various modifications of the copper salt may be calculated at the temperatures at which they are actually formed.

The conversion of the α- into the β-salt at 18·25° C. = 3220 cal., and at 200° it will be 4089 cal., as given by the equation—

$$H - c_\beta(T' - T) = H' - c_\alpha(T' - T) \text{ (see p. 7)},$$

the heat of its formation, and therefore the tendency which it has to form *increases* with the temperature.

The transformation of the β- into the γ-modification is an endothermic reaction, absorbing 1918 cal. as measured at 18·25°, and its being such accounts, no doubt, for the ease with which it reverts to the β-modification unless cooled rapidly (see p. 2), whereas the β-modification being formed in an exothermic reaction, exhibits no tendency to revert to the α-modification from which it is formed (see p. 7).

But here an anomaly arises: at about 300°, the lowest temperature at which the γ-modification appears, its formation will be even more endothermic than at 18·25°; applying the equation given above, *mutatis mutandis*, it will be found to be $-$4031 cal.† when formed from the β-modification, or 459 cal. when formed from the α-modification, the formation of the β- from the α-modification at this same temperature being 4490 cal. In other words, although the tendency to form the β-modification (as measured by the heat development) *increases* continuously with the temperature, and the tendency to form the γ-modification *decreases* with the temperature, yet a certain rise of temperature converts the former into the latter. The only conclusion which can be drawn from this is that the heat development is not the determining factor of this change. We have here a striking exception to Berthelot's "Principe de Travail Maximum" (*Méc. Chem.*, 2, 417), which has of late been attacked to no inconsiderable degree.

* Saturated solutions of copper and potassium sulphates were mixed at 12°. About 48 per cent. of the sulphates present crystallised out in the form of the double salt. On performing a similar experiment with the magnesium sulphate, no crystallisation took place till about 45 per cent. of the water had evaporated, and then it was the *uncombined* salts which separated out. Zinc and nickel sulphates resemble copper sulphate in this respect, whereas those of iron and manganese resemble magnesium sulphate. The formation of the double salt in the liquid appears to be a process requiring a considerable time. In one case, it was found that only 60 per cent. of the total crystals yielded had separated out after 12 hours, and in another case, after 24 hours, 95 per cent.

† According to the experiments on the heat of dissolution this number should be even greater than when based on the direct determination of the specific heats (see p. 7).

III. *An Examination of the Phenol Constituents of Blast-furnace Tar, obtained by the Alexander and McCosh Process at the Gartsherrie Ironworks.* (Part I.)

By Watson Smith, Lecturer in Chemical Technology in the Victoria University, Manchester, with Messrs. J. F. H. Coutts and H. E. Brothers.

A paper was read by one of us before the Society of Chemical Industry (Liverpool Section), December 29th, 1883, "On a Preliminary Examination of Blast-furnace Coal-tar," from the Gartsherrie furnaces, in which Scotch coals are used (mostly unsuitable for coke making). In this paper the following observation was made in the examination of the higher boiling oils (see *Jour. Soc. Chem. Ind.*, 2, 495), when the losses by treatment with sulphuric acid and alkali respectively were determined by suitable measurements. *The oils of higher boiling point contained more compounds absorbed by acids (basic constituents) and less phenol constituents absorbed by soda, than the oils boiling below them.*

It was now determined to ascertain approximately what proportions of crude phenols, and of amido- or basic-constituents, are contained in those portions of the tar-oils analogous to the carbolic-oil and creosote-oil of ordinary coal-tar. For this purpose, known volumes of the oil were repeatedly treated with caustic soda-lye until exhausted o phenol-constituents; the latter were liberated by acid, collected, an measured, with the following results:—

	Per cent. by vol. of phenols obtained.
By the 1st treatment with equal vol. of caustic soda of 1·08 sp. gr.	17·5
By the 2nd treatment with 0·65 of their volume of soda of 1·15 sp. gr.	4·6
By the 3rd treatment with 0·75 of their volume of soda of 1·20 sp. gr.	0·7
By the 4th treatment with 0·65 of their volume of soda of 1·25 sp. gr.	0·3
Total	23·1

In order to determine the percentage of basic constituents present, 1160 c.c. of the blast-furnace tar-oils were shaken for a day with 840 c.c. of dilute sulphuric acid of about 1·2 sp. gr. After standing 12 hours, the aqueous layer was separated, and treated, first with a

certain excess of caustic soda, and then with common salt; after which it was allowed to stand in a graduated jar. The volume occupied by the layer of basic substances was read off, and it was then removed by means of ether; the ethereal solution being heated to expel the ether, and the basic residue again measured. It was observed that though the odour of the crude bases resembled that of the quinoline bases, yet it was by no means so marked in these bases as in the case of the basic oils obtained from ordinary coal-tar oils by a similar process; 1160 c.c. oils by this treatment gave 150 c.c. of crude bases = 11·09 per cent. by volume.

These blast-furnace tars are consequently very rich in phenols, which may be roughly stated to constitute 20 per cent. of their volume. This proportion far exceeds what can be obtained in a similar manner from ordinary coal-tar oils (gas-retort coal-tars), and we would point to this circumstance as being to some extent a confirmation of K. E. Schulze's theory with regard to the probable formation of, at all events, a considerable proportion of the aromatic coal-tar hydrocarbons, by the breaking up at higher temperatures of first-formed phenols into the elements of water and hydrocarbons (see *Annalen*, **227**, 143). In such case, we should expect to meet with intermediate tars, which contain, in predominating quantity, these half-way phenol constituents, if they may so be termed. These blast-furnace tars (and probably to a less extent the Jameson and Aitken coke-oven tar-oils) are of this intermediate character.

If Schulze's theory be correct, amongst these phenols we ought to be able to find those members most nearly corresponding to the hydrocarbons which predominate in what we may term normal coal-tar, produced in gas-retorts at the highest temperatures. For the purpose of testing this question, we have made a careful examination of the blast-furnace tar phenols, with the details and results which follow:—

A rough quantitative fractionation was made of the crude phenols obtained (*Jour. Soc. Chem. Ind.*, **2**, 497) by prolonged agitation of about 14 gallons of the tar-oils of sp. gr. 0·988 with an equal bulk of caustic soda-lye of sp. gr. 1·08, and subsequent treatment of the soda solution with excess of sulphuric acid (2 gallons of dark brown-coloured phenols of sp. gr. 1·07 being obtained); this showed that whereas only 5·63 per cent. by volume distilled over between 180° and 210°, no less than 30 per cent. passed over between 210° and 240°. The results of the fractional distillation were, in fact, as follows:—

	Per cent. by vol.	
Below 190°	1·33	
190—200	0·90	
200—210	3·40	
210—220	6·00	30·7 per cent.
220—230	13·84	
230—240	10·84	
240—250	8·52	
250—260	6·80	
260—270	8·14	18·0 per cent.
270—280	3·65	
280—290	2·66	
290—300	3·72	
300—360	2·88	
360° to coking of residue	13·50	
	91·70	

The portion which distilled over below 180° consisted chiefly of water, and was disregarded. The other fractions, which remained liquid at ordinary temperatures (that distilling from 360° to coking of the residue solidifies to a red semi-solid resin), were now dried by remaining in contact with fused calcium chloride for some time. Each of these fractions was then decanted, and submitted to refractionation, all of such fractions distilling below 300° being separated carefully into sub-fractions of 5° each, whilst those from 300° to 350° were, as far as possible, separated into fractions of 10° each. The fractionations were repeated, and the selections made in the usual way, when it was found that by far the larger portion of the phenols distilled between 210° and 225°. During the distillation of the portions boiling below 300°, much sulphuretted hydrogen was at first evolved, and later on sulphurous acid; at the same time, a considerable deposit of free sulphur was formed in the condensing tubes. This evolution of sulphuretted hydrogen and sulphurous acid with deposition of sulphur, is most marked with the lower boiling portions, and is evidently due to the decomposition of peculiar sulphur compounds, unstable on distillation. After a few distillations, the evolution of gas ceased, and the phenols then possessed a much pleasanter odour. In fractionating the portion distilling from 300° to the coking point of the residue, it was observed that just at the coking point a peculiar decomposition occurred, both hydrocyanic acid and ammonia being evolved, distinctly recognisable by their odours. It is probable that this may be due to the decomposition of peculiar higher nitriles in presence of a limited amount of moisture and hydrogen, ammonia and

hydrocyanic acid being formed. It seems strange at first sight that nitrogenous compounds of this kind should be present in the phenols after the solution in soda and precipitation with acid; but even such a non-basic substance as naphthalene is often found in crude phenols.

For further operations, the final fractions were classified into three groups: (A) All the fractions boiling below 230°; (B) all boiling between 230° and 300°; and (C) all boiling above 300°.

Examination of the Constituents of Group A.

The fractions in this group were distilled until they boiled pretty constantly; each was then placed in a freezing mixture, when that boiling from 180° to 185° at once crystallised to a solid mass, melting again at − 3°. The next fraction showed signs of incipient crystallisation at − 13°. The first consisted chiefly of phenol, $C_6H_5 \cdot OH$, but was not quite pure, as the low melting point shows; it contained small quantities of meta-cresol. A larger proportion of cresol is present in the other fraction refusing to crystallise above − 13°. The examination had not proceeded far before it was found that on dissolving the various fractions in soda, milky solutions were formed, indicating the lingering presence of certain impurities. Their removal was effected by shaking the milky solutions with ether, and separating the ethereal layer by means of a tap-funnel. Sulphuric acid then liberated the pure phenols, which were dried over calcium chloride and refractionated. The solutions of the higher boiling phenols in caustic soda had a blue colour, increasing in depth with the rise in boiling point. So far it was satisfactorily proved that the phenols boiling between 180° and 200° consisted chiefly of phenol, $C_6H_5 \cdot OH$, and the cresols, but that the proportion of cresol to phenol was very much larger than in ordinary crude phenol similarly extracted from gas-tar. It may be interesting, however, to mention that the relative amount of phenol, $C_6H_5 \cdot OH$, in the crude phenols of blast-furnace tar considerably exceeds that found in the crude phenols extracted from the Aitken and Jameson tar-oils (that is, by using for a given volume of the different tar-oils the same proportion of caustic soda solution of the same strength). The following table, based on the results of the fractional distillations of the crude phenols obtained by the same process from blast-furnace tar and from Jameson coke-oven tar, shows as far as such results can do, the similarity of these crude phenols as well as their chief difference, namely, that whereas the blast-furnace product abounds in the phenols boiling between 200° and 230°, that from the Jameson coke-oven tar is rather deficient in them. The relative proportions, however, of the different phenols in the fraction distilling between 230° and 250° are very similar in the two varieties.

Table comparing the Results of Fractionating the Crude Phenols from Blast-furnace and Jameson Coke-oven Tars, the Water being deducted.

Temperature centigrade.	Phenols from blast-furnace tar, per cent.	Phenols from Jameson coke-oven tar, per cent.		
Below 180°	1·4			
„ 210	4·5		5·5	Below 228°
„ 220	6·4			
„ 230	14·3		10·0	235
„ 240	11·5		14·8	250
„ 250	9·1			
„ 260	7·2		9·6	270
„ 270	8·7			
„ 280	3·9			
„ 290	2·8		5·6	300
„ 300	4·0			
„ 360	3·0			
360° to coking point	14·3	Pitch (residue)	26·6	—
Coke and loss	8·9	Loss	14·8	—
	100·0		100·0	

When similar methods of extraction are employed for oils distilling between the same temperatures, from—

1. *Ordinary Lancashire gas-retort coal-tar* ("carbolic oils"), the yield is about 5 per cent. by volume of good crude phenols, containing 65 per cent. (vol.) of a carbolic acid, sufficiently pure to crystallise at ordinary temperatures with ease.

2. *The blast-furnace tar*, the yield was 17·5 per cent. by volume of phenols containing the small quantity of phenol, $C_6H_5 \cdot OH$, indicated in the table just given, and in the results recorded before the table. (By exhaustive treatment with alkali 23·1 per cent. was extracted.)

3. *The Jameson coke-oven tar-oils*, the yield was about 5 per cent., and the amount of phenol, $C_6H_5 \cdot OH$, was extremely small, considerably smaller than that obtained from the blast-furnace tar. (By exhaustive treatment with alkali, about 8 per cent. could be extracted.)

It will be seen how far these results, in the case of the blast-furnace tar, coincide with what we might expect, assuming the truth of Schulze's theory, to the effect that in the formation of aromatic hydrocarbons by the destructive distillation of coal, phenols are primarily formed, and these subsequently suffer disruption at the higher temperatures, yielding water and hydrocarbons of the aromatic series. The Jameson product is scarcely a coal-tar, and may be regarded as a still nearer approach to the shale oils of the paraffin shale distiller.

We should be very slow, however, to decide that the aromatic hydrocarbons are always formed in this way during the destructive distillation of coal, though strongly inclined to believe that phenols are more easily formed first and at lower temperatures than the aromatic hydrocarbons, and also that such phenols by decomposition at the higher temperatures do give rise to a certain proportion of the hydrocarbons. Still, we think it is quite possible that this may be entirely in accordance with facts, and yet that the theories of O. Jacobsen (*Ber.*, 1877, 853), Berthelot (*Compt. rend.*, **62**, 905—947), and Anschütz (*Ber.*, 1878, 1215), as to the synthetic formation of hydrocarbons of the benzene series, and of naphthalene, phenanthrene, and anthracene, may also hold good under special circumstances and conditions. It is needless to point out that were Schulze's theory the only solution of the problem, it would be difficult to account for the amount of benzene in gas-tars, seeing that amongst the phenols so abundantly present in low-temperature coal-tars and oils referred to in this paper, phenol itself is so scantily present. But it will now be necessary to proceed with the description of the results we obtained with the other higher boiling phenols in the group of fractions (A) boiling below 230°.

The portion passing over between 210° and 225°, one of the largest fractions, was distilled over hot zinc-dust or passed over hot iron-borings, the product obtained was distilled, and the distillate shaken with caustic soda solution, to remove any unaltered phenols. The insoluble upper layer, smelling like the ordinary "solvent naphtha" of coal-tar, was then dried over calcium chloride and carefully fractionated. It distilled between 115° and 150°, and apparently, therefore, consisted of a mixture of xylenes with a little toluene, indicating that the material operated on was probably a mixture of xylenols with a little cresol. The result of the fractionation showed that the chief portion of the hydrocarbons obtained distilled between 135° and 145°. The fraction which boiled constantly at 135—145°, and smelt exactly like xylene, was analysed, and the following numbers were obtained :—

	I. per cent.	II. per cent.	Calculated for xylene, C_8H_{10}, per cent.
Carbon......	90·84	90·51	90·56
Hydrogen ...	9·20	9·22	9·43

A vapour-density determination (Victor Meyer's method) gave 3·57 as the result, the calculated vapour-density of xylene being 3·67. The material passed over the hot zinc-dust consisted of a proportionate mixture of the fractions distilling between 205° and 230°. One of the largest of these fractions distilled pretty constantly between 205° and 215°. A portion of this shaken with water gave a

blue colour on addition of a drop of ferric chloride, and an alcoholic solution of the phenol gave with ferric chloride a dark green tint, turning blue on addition of water; unsymmetrical metaxylenol [1 : 3 : 4] boils at 211·5°, and gives the same reactions with ferric chloride. A specimen bought as pure metaxylenol from the firm of Langfeld and Reuter of Rostock, gave the above reactions, and on distilling a portion it was found to distil pretty much as our product did, between 205° and 215°. Seeing that this specimen was prepared from pure materials designed to yield the xylenol in question, it may be considered as sufficiently proved that the substance we examined consisted of metaxylenol [1 : 3 : 4]; and seeing that it composed the chief part of our phenol-product boiling between 205° and 230°, and that the xylenes of gas-tar consist chiefly of metaxylene, we think there is sufficient coincidence between these results and K. E. Schulze's theory, to be of interest, and to render them worthy of record.

Examination of the Constituents of Group B.

The fractions distilling between 230° and 300° were redistilled several times, but no very definite or constant boiling points were attained. A mixture of them was taken and distilled over hot zinc-dust (fine iron-borings were found to answer quite as well), when a product smelling like coal-tar naphtha was obtained. The portion of this boiling below 180° was washed with caustic soda and water, dried over fused calcium chloride, and then fractioned. The portion of this boiling below 180° was washed with caustic soda and water, dried over fused calcium chloride, and again fractioned; the portion boiling pretty constantly between 150° and 175° was taken, but there was too small a quantity of it to admit of making both a combustion and a vapour-density determination; the odour bore a strong resemblance to that of pseudocumene. A vapour-density determination by Victor Meyer's method gave 4·01, whilst the calculated vapour-density for trimethylbenzene is 4·15. Hence the chief phenol constituent present in the fraction named seems to be pseudocumenol. Mesitylol was not likely to have been present at all, at all events in more than traces, since its boiling point is 220°, and the specimen distilled from zinc-dust only commenced to distil at 230°. Pseudocumene, boiling at 240°, would be of course included in this, and thus the trimethylbenzene obtained, as before stated, might be expected to consist of pseudocumene with but traces of mesitylene.

The portion of the reduced product boiling above 180°, was now taken, and was found to have partially solidified to a semi-crystalline mass. The liquid portion was poured off from this, and the crystalline solid residue was washed with caustic soda and then with sul-

phuric acid. It was washed again, dried, and finally distilled. It passed over almost entirely between 205° and 220°, whilst the fraction distilling between 210° and 220°, solidified completely to a white crystalline mass, which readily sublimed on application of gentle heat, yielding beautiful crystalline plates, melting between 70° and 80°. The odour of the substance, and its ready response to Vohl's characteristic reaction, as well as its melting and boiling points, proved it to be naphthalene, and the amount obtained indicates the presence of naphthol* in considerable quantity in the phenols boiling between 220° and 300° from the blast-furnace tar.

Examination of the Constituents of Group C. (Boiling above 300°.)

To remove all traces of hydrocarbons from these fractions, the phenols were each redissolved in strong caustic soda solution, the solution then largely diluted, and afterwards repeatedly shaken with toluene. After completely removing the toluene, sulphuric acid was added, the phenols liberated, collected, dried, and redistilled.

On passing a mixture of these higher boiling fractions twice over red hot zinc-dust, a product was obtained yielding a fair amount of naphthalene, again testifying to the amount of naphthols in the tar. The higher boiling portion of the hydrocarbons consisted of a buttery-yellowish mass, in which we failed to detect any anthracene.

It is proposed to examine this portion further so as to ascertain, if possible, what hydrocarbons do exist in it.

On distilling over red hot zinc-dust or iron-borings, it was observed that the higher boiling group of phenols, C, gave far less deposit of carbon than the lower one in groups A and B.

So far then, we have proved that in the phenols obtained so abundantly from blast-furnace tars (the same remarks will probably be true of the phenols of the Aitken and Jameson coke-oven tars), there are present—

Ordinary phenol....	$C_6H_5{\cdot}OH$.
Cresols...........	$C_6H_4(CH_3){\cdot}OH$ (chiefly metacresol, 1, 3).
Xylenols..........	$C_6H_3(CH_3)_2{\cdot}OH$ (metaxylenol, 1, 3, 4).
Trimethylbenzene-phenols	$C_6H_2(CH_3)_3{\cdot}OH$ (pseudocumenol).
Naphthols	$C_{10}H_7{\cdot}OH$.

The redistilled portions of the phenols boiling above 350° were tested to discover whether any azo-colours of acceptable shades could be obtained from them. For this purpose, sulphanilic acid was diazotised, and the diazobenzenesulphonic acid treated with small

* See also *Ber.*, **16**, Ref., 150; and *Ann.*, **227**, 143 (K. E. Schulze).

quantities of the phenols in alkaline solution; brown and red dyes were obtained, but none of them were of inviting appearance.

It is quite possible, however, that trials of this kind might lead to unsatisfactory results, from the fact that none of the phenols tested could be other than mixed products.

In conclusion, we beg to state that we are far from asserting that nothing but phenols (the homologues of $C_6H_5{\cdot}OH$) are present in the oils examined, and it is quite possible, for example, that phenol-ethers may also be found in them. It is certain that some compounds not found in ordinary gas-tar phenols similarly extracted, are present, for whereas K. E. Schulze (*loc. cit.*), in his examination of the latter was able to isolate from the portions boiling between 230° and 300°, both α- and β-naphthols, we found it quite impossible to obtain them in the crystalline form from our blast-furnace tar-phenols when following Schulze's method. Evidently some oily or resinous phenoloïd bodies obstinately adhered to and accompanied the naphthols and prevented crystallisation.

IV.—*Aluminium Alcohols.* (Part III.) *Aluminium Orthocresylate and its Products of Decomposition by Heat.*

By J. H. Gladstone, Ph.D., F.R.S., and Alfred Tribe, F.I.C., Lecturer on Chemistry in Dulwich College.

Ten years ago (*Chem. Soc. J.*, 1875, 822) we described a reaction, which was subsequently extended, and named "The Aluminium Iodine Reaction" (*Proc. Roy. Soc.*, **30**, 546). By means of this a number of aluminium-derivatives of the alcohols of the series $C_nH_{2n+1}{\cdot}OH$, and $C_nH_{2n-7}{\cdot}OH$ have been prepared.

In a paper published in the Chemical Society's Transactions, 1882, p. 5, we described the products of the action of heat on several of these aluminium alcohols, and more especially on those obtained from aluminium phenylates and para- and meta-cresylates. The general effect of heat on these aluminium compounds is to produce alumina, more or less of the original alcohol, and the corresponding ether, and sometimes a hydrocarbon; but in the cases of the para- and meta-cresylates, they each furnished, in addition, a beautiful pearly compound, crystallising in hexagonal plates of the formula $C_{15}H_{14}O$. These compounds were shown to be isomeric, and they were named provisionally para- and meta-cresyl ketones.

In the present paper, we describe the preparation of orthocresylate of aluminium, and the action of heat upon it, thus completing the study of the destructive distillation of the cresylic aluminium alcohols.

Aluminium Orthocresylate.

The orthocresol employed in this reaction was obtained from Messrs. Kahlbaum. It melted at 31—32°, and boiled at 186°. Kekulé gives 31—31·5° as the melting point, and 185—186° as the boiling point of orthocresol.

Aluminium has no action on orthocresol at ordinary temperatures, and the action is hardly perceptible for a minute or two even at the boiling point of the compound; but after this the action visibly increases, and proceeds in an increasing proportion. As the action progresses, the aluminium foil becomes studded with black specks and patches—doubtless from the uncovering of certain electronegative impurities which, being in juxtaposition with the active metal, probably accounts for the acceleration in the rate of chemical change already referred to. If a few fragments of iodine are dissolved in the cresol when near its boiling point, and aluminium is added, the decomposition takes place at once and proceeds rapidly.

In order to completely substitute aluminium for the basic hydrogen in orthocresol, it was heated with an excess of thin aluminium foil until action ceased. The product, while still fluid, was strained through fine wire gauze in order to separate particles of the metal and impurities. On cooling, it solidified to a black vitreous mass, and gave on analysis 8·56 per cent. of aluminium. The percentage of this metal in a compound of the formula $Al_2(C_7H_7O)_6$ should be 7·89. The following equation would appear to represent the action:—

$$6C_7H_7OH + 2Al = Al_2(C_7H_7O)_6 + 3H_2.$$

The aluminium orthocresylate readily dissolved in benzene, giving a dark-coloured liquid of a greenish tinge. This colour, and the black colour of the substance itself, we have reason to think, are due to a small quantity of some foreign substance. When the benzene solution is exposed to the air, aluminium hydrate separates, probably from the decomposition of the cresylate by atmospheric moisture. Water and alcohol both decompose it rapidly, aluminium hydrate being formed, and probably the criginal cresol.

Action of Heat.

868 grams of aluminium orthocresylate, prepared as described, were heated in a flask fitted with a wide, bent tube. It quickly melted, and

at a high temperature underwent decomposition, the products being alumina, some carbonaceous and tarry matter, and a dark-brown, viscid distillate. This liquid on cooling was found to contain some aluminium hydrates, but little or no solid organic compound, thus differing from the corresponding volatile products of the destructive distillation of the para- and meta-cresylates. The distillate was divided by fractionation into three portions—(*a*) boiling between 140° and 200°; (*b*) boiling between 200° and 300°; and (*c*) boiling above 300°.

Fraction a.—This portion was a liquid of a light yellow colour weighing 65 grams. It readily dissolved for the most part in a solution of potassium hydrate, from which it again separated on neutralisation with hydrochloric acid. The liquid thus separated was dried over calcium chloride. It boiled at 185—186°; its sp. gr. at 18·2° was 1·049; its refractive index for the line A was 1·5373, and for the line H, 1·5851. On heating with aluminium foil and a fragment of iodine, it quickly underwent decomposition with evolution of hydrogen. This fraction, therefore, consisted almost wholly of the original alcohol reconstituted.

Fraction b.—This portion weighed 200 grams, and was of a yellowish-brown colour. It was well shaken with a solution of potassium hydrate, and the residue washed with water and dried over calcium chloride. The liquid obtained was then fractionated some ten times, rejecting at each distillation the small quantities boiling respectively below 200° and above 300°. The product was further fractionated about 20 times, gradually eliminating portions having the greatest range of temperature. In this way a fraction was ultimately obtained (about one-eighth of the whole) which may be supposed to be a fairly pure specimen of the compound, of which (*b*) in a great part consists.

The substance thus isolated was a colourless, moderately mobile liquid, which became slightly yellow on exposure to light. Its boiling point was 272—278°, and at 24·3° its sp. gr. was 1·047; its refractive index for the line A was 1·5638, and for the line H 1·6202. On combustion with oxide of copper and oxygen:—

I. 0·238 gram gave 0·7456 gram CO_2 and 0·1502 gram H_2O.
II. 0·270 ,, 0·8449 ,, 0·1698 ,,

The results expressed in parts per 100 give—

	I.	II.
C	85·43	85·34
H	7·01	6·99

On the determination of its vapour-density, 0·1773 gram gave vapour

= in volume to 20 c.c. (corr.). The numbers give 197·8 for the molecular weight of the substance. Its most probable molecular formula is therefore $C_{14}H_{14}O$.

		Calc. for 100 parts.	Found. Mean.
C_{14}	168	84·84	85·38
H_{14}	14	7·07	7·00
O	16	8·09	7·62 (diff.)
	198	100·00	100·00

The odour of this substance resembles that of phenylic ether—namely, that of the geranium leaf,* but fainter, and is similar to the odour of para- and meta-cresyl ethers. We think we are therefore justified in concluding that the substance is also a cresyl ether. It did not crystallise when surrounded by a freezing mixture, from which it would appear not to be the para-modification already described. It seems also to differ in boiling point and sp. gr. from the metacresylic ether already described in the same way, and to about the same extent as the ortho- differs from the meta-cresylic alcohol. We conclude, therefore, from this, as well as from the origin of the compound, that it is orthocresylic ether.

Cresylic alcohols.	Boiling point.	Sp. gr. at 18·2°.	Specific refraction.	Specific dispersion.
Ortho	185° C.	1·049	0·5122	0·0456
Meta	196—202° C.	1·043	0·5116	0·0454

Cresylic ethers.	Boiling point.	Sp. gr. (at 24°).	Specific refraction.	Specific dispersion.
Ortho	272—278°	1·047	0·5385	0·0266(F–A)
Meta	284—288	1·028	0·5386	0·0266(F–A)

It will be observed that each pair of isomeric compounds is practically identical in specific refraction and dispersion, which gives great confidence in the purity of all four specimens.

Fraction c.—This weighed 185 grams, and consisted of a dark-brown, highly viscous fluid. The portions of *b* boiling above 278°

* This resemblance was so marked, that we examined a specimen of pure essential oil of geranium, in the hopes of finding that it contained our cresyl ether; but it did not. We were equally unsuccessful with the compound known as "Indian geranium."

were added to this fraction, and the whole distilled several times; each time collecting, separately, small quantities of liquid which passed over below 280°, and rejecting other small quantities of a tarry non-distillable substance left in the retort. The distillate ultimately obtained was lighter in colour and much less viscous than the original fluid, and on cooling, and still more on standing for 24—48 hours, deposited small quantities of a yellow crystalline substance. In order to separate this solid from the liquid, rather more than an equal volume of alcohol was added, and then enough ether to dissolve the liquid. This mixture was subjected to a freezing mixture of ice and salt, yielded a small quantity of the crystalline substance, which was removed by filtration. The alcohol and ether were next separated from the liquid substance by distillation, and the residuum distilled, rejecting, as before, portions boiling below 280° and the tarry non-distillable residue. The distillate obtained was again mixed with alcohol and ether, and subjected to a freezing mixture when another portion of the crystalline compound separated. These operations were repeated some 15—20 times, as long as any quantity of the solid could be recovered. The total amount isolated weighed a little less than 2 grams.

In order to purify this substance, it was dissolved in boiling alcohol and recrystallised therefrom some four or five times. It was then slowly distilled, and the distillate again crystallised from alcohol. The body was now lemon-yellow in colour, and consisted of fragments of very thin plates. On combustion with oxide of copper and oxygen, it gave numbers agreeing with the formula $C_{15}H_{14}O$.

	In 100 parts.	
	Found.	Calculated.
Carbon	85·95	85·71
Hydrogen	6·60	6·66
	7·45	7·63 (diff.)
	100·00	100·00

The experience gained in the purification of some of the compounds described in the second part of this research led us to suspect that the lemon-yellow colour of the substance above referred to was occasioned by its admixture with a small quantity of colouring matter. With the object of separating this impurity, the substance was slowly sublimed, when brilliant plates were obtained, but of no very definite form. These were dissolved in hot alcohol, and the solution on cooling deposited diamond- and star-shaped plates free from colour. The quantity of the substance thus purified was too small to allow of further quantitative examination. We have little doubt, however,

but that its composition is expressed by the number given above, and that it has the molecular formula $C_{15}H_{14}O$. Whether the body is identical with either of the so-called ketones obtained from the aluminium meta- and para-cresylates, or is an isomeride bearing the same relation to orthocresol as these compounds bear to their respective alcohols, we have no evidence, physical or chemical, which will enable us to decide, as we attach little or no importance to the difference in crystalline form.

It appears from this investigation that the action of heat on the aluminium orthocresylate is generally similar to the action of heat on the para- and meta-modifications. Each of these compounds has yielded its hydrogen-derivative, or alcohol, the corresponding ether, and a crystalline sublimable compound of the formula $C_{15}H_{14}O$, together with others not isolated. There are, however, one or two points of difference of some interest. Firstly, the different aluminium compounds have yielded very different quantities of distillate, and, still more, very different quantities of the so-called ketones. This is shown in the following table of results:—

	Distillate from 1000 parts.	Solid from 1000 parts.
Aluminium paracresylate	609	106
,, metacresylate	640	20
,, orthocresylate.....	475	2·5

Another point which may perhaps account for the different amounts of distillate, is the different temperatures required to effect destructive distillation of the several aluminium cresylates. This was especially noticed in the case of the para- and ortho-modifications. Besides probably accounting for the difference in the amount of the product, this observation is of interest as showing that a difference exists in the stability of these aluminium isomerides.

V.—*On some New Vanadium Compounds.*

By J. T. BRIERLEY, Dalton Scholar, Owens College.

THESE compounds are formed by the following remarkable reaction. If a blue solution of hypovanadic sulphate be mixed with a colourless solution of an alkaline metavanadate, a dark-green liquid will be produced, and if to this a slight excess of caustic soda is added, the colour of the solution quickly changes to a deep black. From this dark-

coloured solution, well-defined crystalline salts having a purple or dark-green colour and metallic lustre, can be obtained, in which the condition of oxidation of the metal is intermediate between the tetroxide, V_2O_4, and the pentoxide V_2O_5. I have succeeded in preparing five distinct numbers of this group of salts, viz.:—

1. A soluble sodium salt having the composition—

$$2V_2O_4,V_2O_5,2Na_2O + 13H_2O.$$

2. A soluble potassium salt—

$$2V_2O_4,V_2O_5,2K_2O + 6H_2O.$$

3. An insoluble potassium salt—

$$2V_2O_4,4V_2O_5,5K_2O + H_2O.$$

4. A soluble ammonium salt—

$$2V_2O_4,2V_2O_5,(NH_4)_2O + 14H_2O.$$

5. An insoluble ammonium salt—

$$2V_2O_4,4V_2O_5,3(NH_4)_2O + 6H_2O.$$

Intermediate Oxides.

Professor Roscoe observed long ago that when black vanadium trioxide, V_2O_3, is exposed to the air for many months, it absorbs oxygen and moisture from the air, its colour changing to a pale grass-green. On analysing a sample of such an oxide which had been freely exposed to the air for a considerable length of time, I found that its composition, as regards its degree of oxidation, corresponds with that of the insoluble potassium and ammonium salts, viz., $V_2O_4,2V_2O_5 + 8H_2O$.

	Found.	Calculated.
Vanadium	45·08	45·49
Oxygen	33·45	33·19
Water	21·47	21·32
	100·00	100·00

This oxide, dissolved in dilute sulphuric acid and neutralised with caustic potash, yields, when heated, the purple insoluble potassium salt.

Another intermediate dark-green oxide, containing an equal number of molecules of tetroxide and pentoxide, may be obtained by the gentle ignition of the ammonium salt, No. 5. This oxide readily absorbs moisture from the air, its composition then being—

$$3(V_2O_4,V_2O_5) + 8H_2O.$$

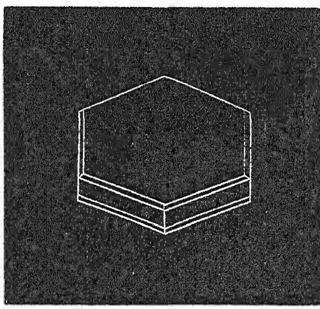
	Found.	Calculated.
Vanadium........	51·83	51·62
Oxygen..........	35·94	36·29
Water	12·23	12·09
	100·00	100·00

This intermediate oxide, V_4O_9, can also be obtained in solution by adding strong sulphuric acid to a hot saturated solution of ammonium metavanadate, and then passing sulphur dioxide through the solution until the liquid attains a green colour. After driving off the excess of sulphur dioxide by boiling, the solution was titrated with permanganate and found to contain vanadium tetroxide and pentoxide in equal molecular proportions. The green-coloured solutions thus obtained may also be prepared by suspending freshly precipitated hydrated vanadium tetroxide in water, adding an insufficient quantity of dilute sulphuric acid to dissolve it, and allowing the turbid liquid to stand several hours. These solutions are very unstable, gradually changing colour from absorption of atmospheric oxygen, passing through all shades of colour, from dark-green to light-brownish yellow.

Intermediate Salts.

1. *Soluble Sodium Salt*, $2V_2O_4,V_2O_5,2Na_2O + 13H_2O$.—In order to prepare this salt, 12 grams of finely powdered vanadium pentoxide is placed in a flask, an excess of a strong solution of sulphur dioxide poured on to it, and the solution heated to the boiling point, small quantities of sulphuric acid being added from time to time. The deep blue solution thus obtained is then well boiled to expel every trace of sulphur dioxide. Six grams of vanadium pentoxide are separately boiled with an excess of caustic soda until completely dissolved. The two solutions are now mixed hot, and caustic soda added to the dark blackish-green liquid until it is slightly alkaline; after standing for a short time, acetic acid should be added to the liquid in very slight excess only, as an excess of caustic soda decomposes the green salt. On filtration after boiling, the filtrate contains the new salt together with sodium sulphate. As these two salts possess nearly the same degree of solubility they cannot be separated by crystallisation; on adding to the cold solution a cold saturated solution of sodium acetate, however, the new vanadium salt is precipitated in black shining crystals. These are deposited in large quantity and of considerable size if the liquid is heated after addition of the acetate, and then allowed to cool. The crystals should be washed with a saturated solution of sodium acetate until the washings are free from sulphuric acid, and the adhering acetate removed by washing with dilute alcohol

until the latter no longer yields an acid distillate. Finally the crystals are dried over calcium chloride. The sodium salt thus obtained consists of black shining plates which, under the microscope, are seen to consist of groups of short hexagonal prisms, and have a sp. gr. of 1·327 at 15° compared with water at 15°. A solution of the pure salt, on slow crystallisation, yields hexagonal plates of considerable size, having the form shown in the figure, and an angle between the faces of the pyramid and prism of 133° 45′. The salt is readily soluble in water, yielding a dark blackish-green solution which, on acidification with a few drops of sulphuric acid, instantly changes to a light grass-green, whilst alkalis restore the black colour, unless an excess be added, when the compound is decomposed with formation of a red-brown solution. The sodium salt is insoluble in strong saline solutions—especially in those of the acetates in the cold; if boiled with potassium or ammonium acetate, purple insoluble salts of these metals are formed.



The quantity of the two oxides of vanadium present was ascertained by titration with a standard permanganate solution, care being taken, in the determination of the tetroxide, to use cold solutions, to displace all air by carbon dioxide, and to use well boiled water for dissolving the salt. The total vanadium was estimated by the same method after complete reduction with sulphur dioxide. In order to estimate the alkaline metal, the vanadium was precipitated as lead salt by basic lead acetate, the excess of lead removed by sulphuretted hydrogen, and the sodium weighed as sulphate.

For the purpose of determining the water of crystallisation, the salt was heated to redness in a combustion-tube in a current of dry air, and the water collected in a weighed calcium chloride tube.

The following are the results obtained :—

	Found.		Calculated. $2V_2O_4,V_2O_5,2Na_2O + 13H_2O$.
	1st preparation.	2nd preparation.	
V_2O_4	37·67	36·80	38·12
V_2O_5	21·19	21·00	20·88
H_2O	26·05	25·34	26·80
Na_2O....	14·15	13·88	14·20
	99·06	97·02	100·00

2. *Soluble Potassium Salt*, $2V_2O_4,V_2O_5,2K_2O + 6H_2O$.—In order to prepare this salt, 20 grams of vanadium pentoxide were reduced by sulphur dioxide, and 10 grams also were converted into potassium metavanadate, the filtered solutions being mixed and caustic potash added to slight alkalinity. The resulting greenish-black liquid was then heated to the boiling point, filtered, mixed with a cold saturated solution of potassium acetate, and the mixed liquids evaporated on the water-bath to a small bulk. On cooling and standing, a mass of small dark crystals separated which, under the microscope, were seen to consist of imperfectly formed octohedrons having a purple colour, mixed with other dark-green four-sided crystals. The mixed crystalline mass was then well washed on a filter with hot water, which dissolved the greenish-black crystals, leaving the purple insoluble salt behind. The dark-green filtrate was, as before, mixed with a concentrated solution of potassium acetate, heated until the separated crystals redissolved, and the solution left to cool. On standing, fine greenish-black crystals were deposited from which all trace of potassium sulphate was removed by continued washing with weak alcohol. This compound has a sp. gr. of 1·389 at 15°, compared with water at 15°.

Analysis of this salt gave the following:—

	Found.			Calculated. $2V_2O_4,V_2O_5,2K_2O + 6H_2O$.
	1st preparation.	2nd preparation.		
V_2O_4	42·02	40·83	40·16	41·04
V_2O_5	23·54	23·90	22·58	22·48
H_2O	11·11	12·82	13·84	13·31
K_2O	21·04	21·21	21·58	23·17
	97·71	98·76	98·16	100·00

Preparation No. 1 contains 5 mols. H_2O.

3. *Insoluble Potassium Salt*, $2V_2O_4,4V_2O_4,5K_2O + H_2O$.—The purple insoluble salt above mentioned can be easily obtained pure from the mother-liquors of the sodium salt. This dark-green solu-

tion containing sodium acetate and sulphate is heated and filtered hot, to the hot liquid some solid potassium acetate is added, and the whole is well boiled. Small crystals having a metallic lustre soon form on the surface of the liquid, and, if the boiling be continued, the whole of the soluble sodium salt may thus be converted into the insoluble potassium compound. The sp. gr. of this salt is 1·213 at 15° compared with water at 15°. In order to determine the potassium in this insoluble salt, it was oxidised with strong nitric acid, and the pentoxide converted into the ammonium salt; this was then precipitated with lead acetate as before, and the alkali weighed as sulphate.

	Found.		Calculated.
	1st preparation.	2nd preparation.	$2V_2O_4,4V_2O_5,5K_2O + H_2O$.
V_2O_4	20·75	22·81	21·48
V_2O_5	47·47	45·98	47·05
K_2O	28·24	29·82	30·32
H_2O	2·26	1·17	1·15
	98·72	99·78	100·00

The amount of water in Preparation No. 1 corresponds with 2 mols H_2O, whilst that in No. 2 agrees with 1 mol. H_2O.

4. *Soluble Ammonium Salt*, $2V_2O_4,2V_2O_5,(NH_4)_2O + 14H_2O$.—This salt is formed by boiling vanadium pentoxide with ammonia until solution takes place, reducing two-thirds of the resulting solution to V_2O_4, mixing this with the unreduced third, and adding ammonia to slightly alkaline reaction. A dark-green solution of the above ammonium salt is thus formed; this cannot be boiled, as the salt is thereby converted into the insoluble compound. By adding acetic acid to the solution until faintly acid, and then alcohol, and allowing the mixture to stand after well shaking, a black crystalline precipitate separates. The supernatant liquid is decanted, and the precipitate thrown on a filter, and washed with a mixture of equal volumes of alcohol and water until free from sulphuric acid. The salt thus obtained is then dried over calcium chloride. It consists of greenish-black crystals which are very unstable, readily absorbing oxygen from the air. In order to determine the ammonia, the salt placed in a platinum boat was heated in a combustion-tube, and the ammonia collected and weighed as platinochloride. Analysis gave :—

	Found. 1st preparation.	Calculated.
V_2O_4	33·20	33·23
V_2O_5	35·62	36·43
$(NH_4)_2O$.	5·67	5·19
H_2O*	25·51	25·15
	100·00	100·00

* Water by difference.

5. *Insoluble Ammonium Salt*, $2V_2O_4,4V_2O_5,3(NH_4)_2O + 6H_2O$.—The foregoing soluble salt is readily converted into this insoluble compound by adding ammonium chloride to its solution rendered alkaline by ammonia, and gently heating the liquid for some time. Small purple crystals having a metallic lustre separate out—first on the sides of the vessel, and afterwards on the surface of the hot liquid. It is not necessary for this purpose to prepare the pure soluble ammonium salt, as the dark-green liquid obtained by mixing equal parts of solutions of V_2O_4 and of ammonium metavanadate readily yields this salt when rendered alkaline with ammonia and heated. The crystalline precipitate is well washed with hot water until it is seen under the microscope to be perfectly homogeneous.

It crystallises in small purple octagonal plates, of a metallic lustre, and yields a brown powder. Its sp. gr. at 15° is 1·335 compared with water at 15°. Analysis gave :—

	Found. 1st preparation.	Found. 2nd preparation.		Calculated. $2V_2O_4,4V_2O_5,3(NH_4)_2O + 6H_2O$.
V_2O_4	25·64	24·77	25·15	25·09
V_2O_4	55·48	55·29	55·42	55·01
$(NH_4)_2O$..	11·68	12·40	11·51	11·76
H_2O*	7·20	7·54	7·92	8·14
	100·00	100·00	100·00	100·00

* Water by difference.

In concluding my paper, I must thank Mr. Harden, of Owens College, for kindly confirming several of my results.

VI.—*On the Vapour-pressures of Mercury.*

By William Ramsay, Ph.D., and Sydney Young, D.Sc.

In a recent paper in the Transactions (1885, 640—657), we described a method by which constant known temperatures could be maintained with great exactitude. In the tables which conclude that paper, Regnault's determinations of the vapour-pressures of mercury have been accepted as correct; on revision, however, they appear to be by no means so trustworthy as most of his work. In vol. 26 of the *Mémoires de l'Académie* Regnault quotes results described in vol. 21, p. 502, and uses these results for determining the formula devised by him to express the relation between temperature and pressure at low temperatures. On reference to vol. 21, it is evident from Regnault's own remarks, that he placed little confidence in the accuracy of his results. His words are as follows:—"Ces deux séries d'expériences différent notablement quand on compare les valeurs relatives qu'elles donnent pour les forces élastiques de la vapeur mercurielle; mais les différences absolues que l'on trouve entre les forces élastiques sont réelement très-petites, et de l'ordre de l'incertitude des observations. Les expériences précédentes suffisent neanmoins pour montrer que la tension de la vapeur de mercure à 100° est d'environ 0·5 mm.; et qu'à la température de 50°, elle s'élève à peine à 0·1 mm. Elle est donc à peu près négligeable au dessous de 50°." These words refer to temperatures below 100°. In a footnote he proceeds—"J'ai fait quelques déterminations de la tension de vapeur du mercure à des températures plus élevées, en chauffant le ballon dans un bain d'huile. Vers 200° les expériences sont devenues évidemment fautives, par suite de la distillation du mercure. Quoiqu'il en soit, voici les nombres que j'ai obtenu: *il convient de ne les regarder que comme des approximations.*" (The italics are ours.) His numbers then follow. They are the results of eleven readings, and these are all which he gives at temperatures below 250°. He also refers in vol. 26 to four determinations given in vol. 21, p. 230, made at the boiling point of mercury under atmospheric pressure, for the purpose of comparing his mercurial and air thermometers. His method in this instance differed essentially from the other methods employed; it consisted in heating an air reservoir terminating in a capillary tube in the vapour of mercury boiling under atmospheric pressure, sealing the tube, and when cold, breaking the point off under mercury, and measuring the contraction of the air. These four experiments gave fairly concordant results, but owing to an evident misquotation in vol. 26, it is not

quite certain to what pressures his symbols h and h_0 refer, as from h the mean of the four determinations would give the pressure 767·43, while from h_0 765·29 is the mean. But as the temperatures themselves differ by nearly 2° at the same pressure, this slip is an unimportant one. At higher pressures, Regnault employed a large iron still, containing 50 kilos. of mercury, into which dipped an iron tube containing the air thermometer. By applying pressure from an air reservoir, the boiling point of the mercury was regulated and observed. He states that the temperature was observed as soon as it had become constant, and the observations were repeated until it began to rise, by which time the greater part of the mercury had distilled over. He directs attention to the fact that, using this method, the temperatures are those of the boiling liquid, and not of the vapour. During distillation, the noise of the bumping was compared to blows of a hammer on an anvil. That these results cannot be relied on is shown by those referring to the atmospheric pressure, where a fall of 7·4 mm. in pressure corresponds to a rise of temperature of 1·86°; and the mean temperature (about 355·4°) by no means corresponds with that obtained by the method previously described (358·5°). It is obvious that good results cannot be anticipated under such conditions.

The importance of a correct knowledge of the vapour-pressures of mercury is evident, when it is considered that they enter into all calculations of the determinations of vapour-pressures of liquids by the usual method at high temperatures; and that they must be allowed for in determining vapour-densities by Hofmann's apparatus. Moreover, it is probable that thermometers based on a knowledge of the vapour-pressure of mercury will become available for accurate determinations of high temperatures.

Owing to the discovery of certain relations between the vapour-pressures of different substances, which are described in the *Philosophical Magazine* for December, 1885, and January, 1886, we have been able, with small expenditure of time and labour, to obtain results which we think will be generally accepted as correct. Before describing the experiments, a short description of the generalisations may render the process intelligible. Although some of these apparently have little connection with the matter in question, yet from thermodynamical considerations, they are so interlaced, that we deem it advisable to state them all. For detailed description and proof of the following statements, we would refer to the articles already mentioned.

1. The amount of heat required to produce unit increase of volume in the passage from the liquid to the gaseous state at the boiling point under normal pressure, is approximately constant for all substances.

2. If the amounts of heat required to produce unit increase of volume in the passage from the liquid to the gaseous state be compared at different pressures for any two bodies, then the ratio of this amount at the boiling point under a pressure p_1 to the amount at another pressure, p_2, is approximately constant.

3. It appears probable, from the few data at present available, that if a diagram be constructed in which the ratios at the same pressure between the heats of vaporisation of two liquids, at various pressures, the same for both, form the abscissæ, and the absolute temperatures of one of the two liquids, corresponding to those vapour-pressures, form the ordinates, then the points representing the relations between these ratios and the absolute temperatures will lie in a straight line.

4. The products of the numbers representing the absolute temperature into the increase of pressure per unit rise of temperature at those temperatures, are approximately the same for all substances at the same vapour-pressure; but the differences are real and are not due to error of experiment or calculation.

5. The rate of increase of this product with rise of pressure is very nearly constant for all bodies.

6. The deviation from constancy presents the following relations:—If a diagram be constructed in which the ratios at definite pressures of the product referred to in (4) for any two substances be made the abscissæ, and the absolute temperatures of one of the bodies at corresponding vapour-pressures be made the ordinates, then the points representing the relations of these two quantities will fall in a straight line.

7. A relation exists between the ratios of the absolute temperatures of all bodies, whether solid or liquid, whether stable or dissociable, which may be expressed in the case of any two bodies by the equation $R' = R + c(t' - t)$; where R is the ratio of the absolute temperatures of the two bodies, corresponding to any vapour-pressure, the same for both; R′, the ratio at any other pressure, again the same for both; c, a constant, which may equal 0 or a small plus or minus number; and t' and t the temperatures (absolute or centigrade) of one of the bodies corresponding to the two vapour-pressures.

When $c = 0$, $R' = R$, or the ratio of the absolute temperatures is a constant at all pressures; and when $c > 0$, or $c < 0$, its value may readily be determined either by calculation, or graphically by representing the (absolute) temperatures of one of the two bodies as ordinates, and the ratio of the absolute temperatures at pressures corresponding to the (absolute) temperatures of that body as abscissæ. It is found in all cases that points representing the relation of the ratio of the absolute temperatures of the two bodies to the (absolute) temperature of one of them fall in a straight line.

On comparing such relations for different substances of which the vapour-pressures had been accurately determined, in twenty-three cases, this relation was found to hold absolutely; for on calculating by means of this *ratio* the *absolute temperatures* of *these substances* corresponding to given pressures, the differences observed between calculated and experimental results fall well within the limits of experimental error. On using Regnault's determinations of the vapour-pressures of mercury, the case was different. Here a curve, instead of a straight line, was obtained. Now it is evident that if satisfactory proof can be given that certain temperatures, sufficiently far removed from each other, when compared with the ratios between these absolute temperatures of mercury and some other liquid of known vapour-pressure, *e.g.*, water, give points which fall in a straight line, the value of c is calculable, and as a consequence, the whole vapour-pressure curve of mercury. Mercury also formed the only exception to statements (5) and (6).

The temperatures chosen were—(1) the boiling point of methyl salicylate under atmospheric pressure; (2) the boiling point of bromonaphthalene under a pressure of 612·8 mm.: (3) the same under a pressure of 756·2 mm.; (4) more reliance is to be placed on the boiling point of mercury under atmospheric pressure, determined by Regnault, described in vol. 21 of the *Mémoires*, as the method he adopted seems to deserve greater confidence than his later method; and the mean of his four results may be taken as fairly correct; (5) the boiling point of sulphur under atmospheric pressure, determined by Regnault. For the accuracy of our knowledge of the first three of these temperatures reference must be made to the Transactions (1885, p. 640 *et seq.*).

Regnault determined the vapour-pressures of sulphur, using an apparatus similar to that with which he determined the vapour-pressures of mercury. He did not find it necessary to fill the still with liquid sulphur, and the boiling took place quietly, without bumping. He appears to place more reliance on his determinations of the vapour-pressures of sulphur than on those of mercury; and this conclusion is borne out by our experience; for on comparing the vapour-pressures of sulphur with those of carbon disulphide, the ratios of the absolute temperatures form with the absolute temperatures of carbon disulphide, or sulphur, a straight line, when considered as described in statement (7), and the results agree remarkably well with statements (4), (5), and (6). It is obvious that the temperature of the boiling point of sulphur under atmospheric pressure really amounts to an indirect reading of Regnault's air thermometer; and for the above-mentioned reasons we believe that the temperature in this case is correct.

For the determinations of the vapour-pressure of mercury, the process adopted in our late experiments was employed; and the apparatus is represented in a woodcut on p. 643 of the Transactions for 1885, modified as described on p. 651. A description is therefore unnecessary here.

(1.) The detailed results are as follows:—

Closed limb of apparatus.	Open limb of apparatus.	Δ.	Δ at 0°.	Pressure A at 0°.	Pressure B at 0°.	Vapour pressure of mercury.	Mean.
703·8	704·5	− 0·7	−0·7	34·9	35·1	34·3	34·4
704·2	705·0	− 0·8	−0·8	35·2	35·2	34·4	
701·1	708·0	− 6·9	−6·65	—	41·05	34·4	
704·3	704·1	+ 0·2	+0·2	34·1	34·2	34·45	

Note.—Two gauges and barometers were used, lettered A and B respectively. The mean reading of the two was taken.

The pressure under which the methyl salicylate boiled was 746·95 mm. (reduced to 0°), and the corresponding temperature 222·15°. The mean observed vapour-pressure of mercury at this temperature is accordingly 34·4 mm.

(2) and (3.) The detailed results of our observations with bromonaphthalene are given in our previous paper (*loc. cit.*). The numbers are as follows:—

Pressure of bromonaphthalene vapour.	Pressure of mercury vapour.	Temperature from Regnault's data.
756·2 mm.	157·15 mm.	280·6°
612·8 „	124·35 „	270·35°.

These temperatures are calculated from Regnault's formula for the vapour-pressures of mercury, and were made use of in determining the position of the curve representing the relations of temperature to pressure for bromonaphthalene. It was noticed at the time that this curve would not pass through both points representing the temperatures of the bromonaphthalene; and as other readings had been taken with a mercury thermometer previously compared with an air thermometer, confirming the lower temperature, it was judged right to construct the curve on this basis. Reading then from the curve we adopted, the higher temperature becomes 280·2°, instead of 280·6°. The justice of this correction has since been confirmed by a study of the relations between the absolute temperatures of bromonaphthalene and water.

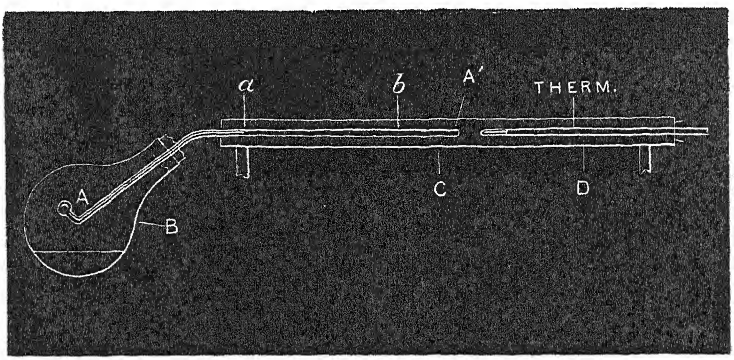
(4.) The relations obtained for mercury at the atmospheric pres-

sure by Regnault have already been considered. They are as follows :—

Temperature.	H_1.	H_0.
358·46°	769·59 mm.	770·27 mm.
357·48	768·40 ,,	766·76 ,,
359·27	768·08 ,,	766·11 ,,
358·68	763·65 ,,	758·02 ,,

H_1 and H_0 are the barometric heights at the moment of closing the air thermometer, and of breaking the point off under mercury; but it is uncertain from the text which symbol is to be used for the one and which for the other. The mean temperature is 358·47°; the mean of h_1 is 767·43 mm.; and the mean of h_0, 765·29 mm.

(5.) In order to determine the vapour-pressure of mercury at the boiling point of sulphur, a new form of apparatus was employed, which is shown in the accompanying figure.



The apparatus AA′ is constructed of barometer tubing of small bore. At the end A is blown a bulb so adjusted as regards size that the volume of the bulb is approximately equal to that of the horizontal portion of the stem, and when cold, containing mercury to the mark *a*. B is a vessel containing sulphur; in one experiment this was a flask, as shown; in the other, a wide test-tube. On applying heat, the sulphur vapour could be caused to completely surround the bulb A. The mouth of the flask was loosely closed with cotton-wool, to prevent escape of sulphur vapour, or the formation of air currents. C is a jacketing tube in the form of a Liebig's condenser, whereby the horizontal portion of AA′ could be maintained at a constant known temperature, shown by the thermometer D.

The tube AA′ was first graduated in millimetres from about *a* to the end; it was then exhausted, filled with mercury, and repeatedly

boiled out under atmospheric pressure, until air bubbles ceased to come off from the glass. The end A′ was next drawn out to a capillary tube, and was exhausted repeatedly with a Sprengel's pump, dry air, which had stood in contact with phosphorus pentoxide for some time, being admitted after each exhaustion. While the capillary tube was still connected with a small drying tube of pentoxide, the tube AA′ was placed in a vertical position in a wide tube through which a current of water of constant known temperature ran; the capillary end of AA′ projected just above the surface of the water. The temperature of the water and the atmospheric pressure were then read, and the capillary was sealed, the position of the mercury in the tube being noted at the same moment. From these data, the volume of the air at known temperature and pressure was subsequently ascertained. The apparatus was then arranged as shown in the figure, and the sulphur made to boil. The ebullition took place quietly and easily, and thin deposit of liquid sulphur on the sides of the flask made it certain that the vapour was not superheated. Had this not been the case, the bulb would have been surrounded with asbestos. When the mercury in the bulb had become hot, it was driven by the pressure of its vapour nearly out of the bulb, and was forced along the horizontal portion of the tube, as far as *b*, compressing the air. The position of *b* was then read, and the temperature of the water in the jacket C was noted. The barometric pressure was also read, so as to determine the temperature of the sulphur vapour. When cold, the tube was broken close to the bend, and calibrated by weighing with mercury. The pressure of the mercury vapour in the bulb is equal to that of the air in the gauge, plus the pressure of a column of mercury equal to the vertical distance between the level of the mercury in the bulb and that in the horizontal portion of the tube, this column being corrected for temperature.

The detailed results are as follows:—

I. (1.) Air at atmospheric pressure:—

Temperature.	Pressure (reduced to 0°).	Volume.
16·20°	743·7 mm.	0·91690 c.c.

(2.) Air at high pressure:—

Temperature.	Volume.
16·60°	0·24440 c.c.

Pressure calculated from above data, 2794·0 mm.

(3.) Column of mercury heated to 450°, 57 mm.

" " " about 100°, 51 mm.

These reduced to 0° become 52·8 mm. and 50·1 mm. respectively.

The total pressure of the mercury vapour is therefore 2794 + 52·8 + 50·1 = 2896·9 mm.

(4.) The barometric pressure when the sulphur was boiling was 742·6 mm. (reduced to 0°), and the corresponding temperature was 447·0°.

II. (1.) Air at atmospheric pressure :—

Temperature.	Pressure.	Volume.
16·24°	752·3 mm.	0·53546 c.c.

(2.) Air at high pressure :—

Temperature.	Volume.
15·40°	0·14385 c.c.

Pressure calculated from above data, 2791·0 mm.

(3.) Column of mercury heated to 450°, 52·5 mm.

„ „ „ about 100°, 66·0 mm.

These reduced to 0° become 48·6 mm. and 64·9 mm. respectively. The total pressure of the mercury vapour is therefore 2791 + 48·6 + 64·9 = 2904·5 mm.

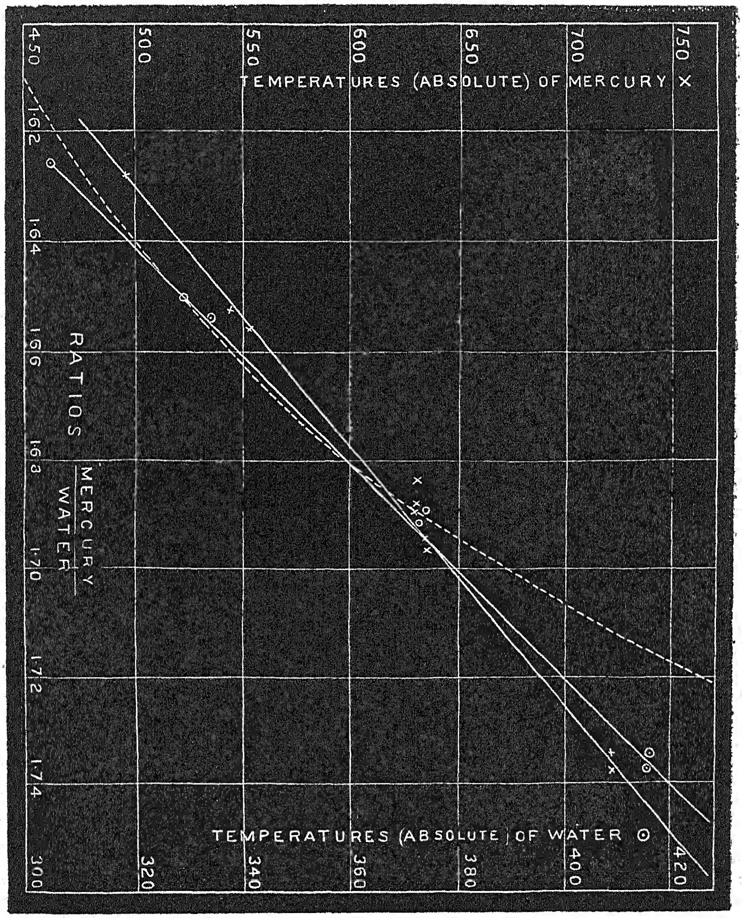
(4.) The barometric pressure when the sulphur was boiling was 754·4 mm. (reduced to 0°), and the corresponding temperature was 448·0°.

The whole of these results are shown in the following table :—

Temperature (centigrade).	Temperature (absolute).	Pressure.	Absolute temperature of water at pressure p.	Ratio of absolute temperature.
222·15°	495·15°	34·40 mm.	304·5°	1·6262
270·30	543·30	124·35 „	329·2	1·6504
280·20	553·20	157·15 „	334·2	1·6553
358·46	631·46	h_1 769·59 „	373·35	1·6913
		h_0 770·27 „	373·37	
357·48	630·48	h_1 768·40 „	373·30	1·6889
		h_0 766·76 „	373·25	1·6892
359·27	632·27	h_1 768·08 „	373·29	1·6938
		h_0 766·11 „	373·22	1·6941
358·68	631·68	h_1 763·65 „	373·13	1·6930
		h_0 758·02 „	372·93	1·6938
447·0	720·0	2896·9 „	415·26	1·7338
448·0	721·0	2904·5 „	415·36	1·7359

The accompanying diagram, in which the ratios are represented as abscissæ, and the absolute temperatures of mercury in one case and of water in the other are the ordinates, represents the results obtained.

The ratios calculated from Regnault's determinations give the dotted curve with absolute temperatures of water as ordinates.



It will be noticed that in each case a straight line can be drawn through all the points. The value of c, if the temperatures of mercury are chosen as ordinates, is 0·0004788; if those of water are chosen, it is 0·0009792.

The calculations of the vapour-pressures of mercury from these two constants give slightly different results; but the difference within the limits of temperature given in the ensuing tables is unimportant, although at higher temperatures it might become considerable. It was more convenient to employ the constant derived from the abso-

lute temperatures of mercury; and we now proceed to show the method of calculation.

A point was read from the straight line, giving the ratio at any one temperature. The absolute temperature of water was calculated from the ratio. The vapour-pressure of water corresponding to this temperature is the same as that of the mercury, inasmuch as the ratios refer to equal pressures. Thus, at an absolute temperature of mercury of 508°, the ratio as read from the line was 1·6331. The absolute temperature of water was therefore $\frac{508}{1 \cdot 6331} = 311 \cdot 06°$. The vapour-pressure of water at 311·06°, ascertained from Regnault's tables is 49·466 mm., and this is therefore the vapour-pressure of mercury at an absolute temperature of 508°. The ratios corresponding to other absolute temperatures of mercury were calculated from the equation $R' = R \pm c(t' - t)$, the value of R being 1·6331, as given above. Of course other ratios might have been read from the straight line; but it seemed better to employ the factor 0·0004788 in the calculation.

The data employed and the results of this calculation are as follows:—

Temperature (centigrade).	Absolute temperature of mercury.	Ratio.	Absolute temperature of water.	Vapour-pressure.
135°	408°	1·585220	257·38°	1·409 mm.
140	413	1·587614	260·14	1·754 ,,
145	418	1·590008	262·89	2·172 ,,
150	423	1·592402	265·64	2·680 ,,
155	428	1·594796	268·37	3·287 ,,
160	433	1·597190	271·10	4·013 ,,
165	438	1·599584	273·82	4·879 ,,
170	443	1·601978	276·53	5·904 ,,
175	448	1·604372	279·24	7·116 ,,
180	453	1·606766	281·93	8·535 ,,
185	458	1·609160	284·62	10·204 ,,
190	463	1·611554	287·29	12·137 ,,
195	468	1·613948	289·98	14·403 ,,
200	473	1·616342	292·64	17·015 ,,
205	478	1·618736	295·30	20·028 ,,
210	483	1·621130	297·95	23·482 ,,
215	488	1·623524	300·59	27·447 ,,
220	493	1·625918	303·22	31·957 ,,
225	498	1·628312	305·84	37·083 ,,
230	503	1·630706	308·46	42·919 ,,
235	508	1·633100	311·06	49·466 ,,
240	513	1·635494	313·67	56·919 ,,
245	518	1·637888	316·26	65·241 ,,
250	523	1·640282	318·85	74·592 ,,
255	528	1·642676	321·42	85·010 ,,
260	533	1·645070	324·00	96·661 ,,

Temperature (centigrade).	Absolute temperature of mercury.	Ratio.	Absolute temperature of water.	Vapour-pressure.
265°	538°	1·647464	326·55°	109·556 mm.
270	543	1·649858	329·11	123·905 ,,
275	548	1·652252	331·66	139·802 ,,
280	553	1·654646	334·21	157·378 ,,
285	558	1·657040	336·75	176·733 ,,
290	563	1·659434	339·28	197·982 ,,
295	568	1·661828	341·80	221·251 ,,
300	573	1·664222	344·31	246·704 ,,
305	578	1·666616	346·81	274·443 ,,
310	583	1·669010	349·31	304·794 ,,
315	588	1·671404	351·80	337·753 ,,
320	593	1·673798	354·28	373·528 ,,
325	598	1·676192	356·75	412·249 ,,
330	603	1·678586	359·22	454·277 ,,
335	608	1·680980	361·68	499·656 ,,
340	613	1·683374	364·14	548·715 ,,
345	618	1·685768	366·59	601·583 ,,
350	623	1·688162	369·04	658·515 ,,
355	628	1·690556	371·48	719·772 ,,
360	633	1·692950	373·91	785·107 ,,
365	638	1·695344	376·33	855·223 ,,
370	643	1·697738	378·75	930·335 ,,
375	648	1·700132	381·16	1010·47 ,,
380	653	1·702526	383·56	1096·22 ,,
385	658	1·704920	385·95	1186·67 ,,
390	663	1·707314	388·34	1283·71 ,,
395	668	1·709708	390·72	1386·60 ,,
400	673	1·712102	393·09	1495·60 ,,
405	678	1·714496	395·45	1611·19 ,,
410	683	1·716890	397·81	1733·79 ,,
415	688	1·719284	400·16	1863·36 ,,
420	693	1·721678	402·50	2000·21 ,,
425	698	1·724072	404·85	2145·57 ,,
430	703	1·726466	407·19	2298·80 ,,
435	708	1·728860	409·51	2459·41 ,,
440	713	1·731254	411·83	2628·79 ,,
445	718	1·733648	414·15	2807·53 ,,
450	723	1·736042	416·47	2996·06 ,,
455	728	1·738436	418·77	3192·69 ,,
460	733	1·740830	421·07	3399·50 ,,
465	738	1·743224	423·36	3616·22 ,,
470	743	1·745618	425·65	3843·68 ,,
475	748	1·748012	427·92	4080·10 ,,
480	753	1·750406	430·18	4327·14 ,,
485	758	1·752800	432·44	4585·95 ,,
490	763	1·755194	434·70	4856·74 ,,
495	768	1·757588	436·96	5139·89 ,,
500	773	1·759982	439·21	5434·99 ,,
505	778	1·762376	441·45	5741·86 ,,
510	783	1·764770	443·67	6059·16 ,,
515	788	1·767164	445·90	6391·49 ,,
520	793	1·769558	448·12	6736·60 ,,

In calculating pressures below 4·6 mm., Regnault's formula

expressing the relation between temperature and pressure of water between 0° and 100° has been employed.

As it was impossible to calculate the vapour-pressure of mercury below 135°, owing to our ignorance of the vapour-pressure of water at low temperatures; and as a knowledge of the lower vapour-pressures of mercury is necessary, the constants of a formula of the form employed by Regnault in calculating the vapour-pressures of water below 0° were calculated. The formula is—

$$\log p = a + b\alpha^t.$$

In calculating this formula, the temperatures and pressures made use of in determining the value of the constants were as follows:—

Temperatures.	Pressures.
160°	4·013 mm.
220	31·957 ,,
280	157·378 ,,

The constants are therefore—

$$a = 4{\cdot}493745 \qquad \log b = 0{\cdot}5899797$$
$$b = -\ 3{\cdot}890276.$$
$$t = t^\circ\ \mathrm{C.} - 160 \qquad \log \alpha = \bar{1}{\cdot}9980929.$$

The table which follows shows the vapour-pressures of mercury at temperatures below 160°, calculated as above described.

Temp.	Pressure.	Temp.	Pressure.	Temp.	Pressure.
40°	0·008 mm.	100°	0·270 mm.	140°	1·763 mm.
50	0·015 ,,	110	0·445 ,,	145	2·181 ,,
60	0·029 ,,	120	0·719 ,,	150	2·684 ,,
70	0·052 ,,	130	1·137 ,,	155	3·289 ,,
80	0·092 ,,	135	1·419 ,,	160	4·013 ,,
90	0·160 ,,				

As these numbers are extrapolated from 220°, it appeared necessary to control them by a determination at a lower temperature. The vapour-pressure of mercury was therefore directly determined at the boiling point of chlorobenzene under a pressure of 754·2 mm., corresponding to a temperature of 131·8°, by the method employed for its determination at the boiling point of methyl salicylate. Twenty-three readings were taken, the level of the mercury in the vapour-pressure tube being altered from time to time. The mean result was 1·58 mm.; the mean probable error was 0·14 mm. The calculated pressure is 1·24 mm.; but we think that the experimental result is as

close as can be expected from the very small amount to be measured, and we regard it as a sufficient confirmation of the accuracy of the table given above. At 132° Regnault's pressure is 2·30 mm., and this is manifestly too high.

In order to afford data whereby the temperatures of mercury vapour used as a jacket may be easily ascertained from the read pressure, we append a table of the vapour-pressures for each degree centigrade. This table is to be substituted for the one published in the Trans., 1885, p. 656.

The results given were smoothed by the method of differences, and each degree was calculated by differences.

Temp.	Pressure.	Temp.	Pressure.	Temp.	Pressure.
270°	123·92 mm.	301°	252·18 mm.	332°	472·12 mm.
271	126·97 „	302	257·65 „	333	481·19 „
272	130·08 „	303	263·21 „	334	490 40 „
273	133·26 „	304	268·87 „	335	499·74 „
274	136·50 „	305	274·63 „	336	509·22 „
275	139·81 „	306	280·48 „	337	518·85 „
276	143·18 „	307	286·43 „	338	528·63 „
277	146·61 „	308	292·49 „	339	538·56 „
278	150·12 „	309	298·66 „	340	548·64 „
279	153·70 „	310	304·93 „	341	558·87 „
280	157·35 „	311	311·30 „	342	569·25 „
281	161·07 „	312	317·78 „	343	579·78 „
282	164·86 „	313	324·37 „	344	590·48 „
283	168·73 „	314	331·08 „	345	601·33 „
284	172·67 „	315	337·89 „	346	612·34 „
285	176·79 „	316	344·81 „	347	623·51 „
286	180·88 „	317	351·85 „	348	634·85 „
287	185·05 „	318	359·00 „	349	646·36 „
288	189·30 „	319	366·28 „	350	658·03 „
289	193·63 „	320	373·67 „	351	669·86 „
290	198·04 „	321	381·18 „	352	681·86 „
291	202·53 „	322	388·81 „	353	694·04 „
292	207·10 „	323	396·56 „	354	706·40 „
293	211·76 „	324	404·43 „	355	718·94 „
294	216·50 „	325	412·44 „	356	731·65 „
295	221·33 „	326	420·58 „	357	744·54 „
296	226·25 „	327	428·83 „	358	757·61 „
297	231·25 „	328	437·22 „	359	770·87 „
298	236·34 „	329	445·75 „	360	784·31 „
299	241·53 „	330	454·41 „		
300	246·81 „	331	463·20 „		

The result of this investigation, we venture to think, furnishes a most convincing proof of the justice of the generalisations on which it is based.

Addendum.

Since reading the above paper, Professor Herbert McLeod has kindly directed our attention to two memoirs on the same subject, one by Hagen (*Ann. Phys. Chem.*, N.F., **16**, 610), and one by Hertz (*ibid.*, N.F., **17**, 193). The methods employed by both these experimenters in measuring temperature are open to criticism. Hagen's experiments appear to have been conducted with very great care; but the results are abnormal, for he finds a pressure which must be greatly in excess of the truth at low temperatures. Hertz employed a method analogous to ours, and the closeness of the coincidence between his results and ours is remarkable, when it is remembered that ours are extrapolated from measurements at much higher temperatures, the correctness of which was confirmed by their agreement with the relations mentioned in our paper. We think it advisable to reproduce their numbers at low temperatures, comparing them with those of Regnault and ourselves.

Temperature.	Regnault.	Hagen.	Hertz.	Ramsay and Young.
0°	0·02 mm.	0·015	0·00019	—
10	0·0268 ,,	0·018	0·00050	—
20	0·0372 ,,	0·021	0·0013	—
30	0·0530 ,,	0·026	0·0029	—
40	0·0767 ,,	0·033	0·0063	0·008
50	0·1120 ,,	0·042	0·013	0·015
60	0·1643 ,,	0·055	0·026	0·029
70	0·2410 ,,	0·074	0·050	0·052
80	0·3528 ,,	0·102	0·093	0·092
90	0·5142 ,,	0·144	0·165	0·160
100	0·7455 ,,	0·210	0·285	0·270
120	1·5341 ,,	—	0·779	0·719
140	3·0592 ,,	—	1·93	1·763
160	5·9002 ,,	—	4·38	4·013
180	11·000 ,,	—	9·23	8·535
200	19·90 ,,	—	18·25	17·015
220	34·70 ,,	—	34·90	31·957

VII.—*Action of Phosphorus Pentachloride on Ethylic Diethylaceto-acetate.*

By J. William James, University College of South Wales, Cardiff.

The action of phosphorus pentachloride on ethylic acetoacetate was first carefully investigated by Geuther (*Jenaische Zeitschrift*, 4, Heft 4), who found that the ethoxyl-group was displaced by chlorine, giving rise to the chlorides of two isomeric chlorocrotonic acids.

Some years later, Rücker (*Annalen*, **201**, 56) submitted an ethereal monalkylacetoacetate to the same treatment, and again found that the ethoxyl of the carboxyl-group was displaced by chlorine, the product being the chloride of a single monalkylchlorocrotonic acid. Judging from these results, it was to be expected that the action of phosphorus pentachloride on a dialkylacetoacetate would give rise to the formation of the chloride of a dialkylchlorcrotonic acid; this, however, is not the case, the chief result of the reaction being a mono-, and a di-chloro-*substitution product*, together with a small quantity of a monalkylchlorcrotonic ethylic salt, as the following experimental results testify.

100 grams (1 mol.) of ethylic diethylacetoacetate boiling at 205—215° was poured into a flask containing 225 grams of phosphorus pentachloride (2 mols.). No reaction took place at the ordinary temperature or at 100°; the mixture was therefore gently heated in connection with a reflux condenser until all the chloride had dissolved, and was kept boiling gently for some time. The upper end of the condenser contained a calcium chloride tube, which entered a cylinder filled half full of water. A thermometer placed in the vapour of the boiling liquid remained very constant at 85°, so the temperature in the liquid could hardly have been much over 100°. During the reaction, volumes of hydrogen chloride were evolved, and also some ethyl chloride which could be inflamed in the cylinder. After boiling for five hours, the liquid had become pale yellow, and on cooling about 25 grams of unused phosphorus pentachloride crystallised out. The liquid poured off from the crystals was now distilled until the thermometer showed 120°, in order to remove most of the phosphorus oxychloride and trichloride, of which it mainly consisted. The residue, which was now brown in colour, was allowed to cool and poured into cold water; and then, as it could not be boiled under ordinary pressure without undergoing considerable decomposition, it was distilled in a current of steam. The oil which passed over very slowly was heavier than water, and insoluble in it. It was collected in three principal fractions of equal volume (I, II, III). The first drops which distilled possessed a peculiar odour, resembling that of the camphor compounds; this was collected separately, but owing to the small quantity it has not been more closely examined; it boils below 200°, with slight decomposition. The last portion was also collected apart (about 3 c.c., Fraction IV). Each of the above fractions was separated from the water, dried over sulphuric acid, and afterwards analysed.

The aqueous distillate had a strongly acid reaction, but after neutralising with sodium carbonate, evaporating to dryness and exhausting with absolute alcohol, only a small quantity was dissolved, the residue consisting of sodium chloride. The liquid in the flask

also had a strongly acid reaction due to phosphoric and phosphorous acids.

Fraction I.—A portion (*a*) of this slightly yellowish liquid, on distillation, boiled from 210° to 220° with decomposition, hydrogen chloride being given off whilst a dark-brown residue remained in the retort. This distillate was analysed, as was also another portion which had not been distilled (*b*).

(*a*). 0·2685 gram substance produced 0·550 gram CO_2 and 0·2025 gram H_2O.

0·2195 gram heated with CaO gave 0·118 gram AgCl.

(*b*). 0·255 gram substance gave 0·517 gram CO_2 and 0·187 gram H_2O.

0·3145 gram finally produced 0·195 gram AgCl.

	Calculated for $CH_2Cl{\cdot}CO{\cdot}C(C_2H_5)_2{\cdot}COOC_2H_5$.		Found.	
			a.	*b*.
C_{10}	120	54·42	55·86	55·3
H_{17}	17	7·72	8·3	8·14
O_3	48	21·77	—	—
Cl	35·5	16·09	13·3	15·32
	220·5	100·00		

The substance, according to these analyses, consisted mainly of ethylic diethylmonochloracetoacetate slightly contaminated with a compound richer in carbon and hydrogen, probably free from chlorine.

Ethylic diethylchloracetoacetate is a colourless liquid, insoluble in water, and of a pleasant odour. It has a sp. gr. of 1·063 at 15°. It is miscible in all proportions with alcohol, ether, and benzene.

Fraction II.—This might consist of a mixture of the two substances which composed fractions I and III, that is, a mixture of mono- and di-chlorinated ethylic diethylacetoacetate, but also of ethylic ethylchlorcrotonate, $CH_3{\cdot}CCl : C(C_2H_5){\cdot}COOC_2H_5$.

Two chlorine estimations, in two samples separately prepared, gave 21·8 and 21·1 per cent. Cl, which agree pretty well with the amount of chlorine in this last-named ether, but also equally consistently for a mixture of equal numbers of molecules of mono- and di-chlorinated ethylic diethylacetoacetate.

This fraction was consequently again distilled in a current of steam until one-half had passed over, dried over sulphuric acid, and the chlorine determined.

Fraction II*a*.

0·288 gram substance produced 0·200 gram AgCl = 17·1 per cent. Cl.

Fraction II*b*.

0·277 gram substance produced 0·265 gram AgCl = 23·6 per cent. Cl.

Calculated for ethylic diethylmonochloracetoacetate 16·1 per cent.

Calculated for ethylic diethyldichloracetoacetate 27·8 per cent.

Presuming that fractional distillation in a current of steam can be carried out with a fair amount of exactitude,* these results tend to show that a compound was present which was neither the monochloro- nor dichloro-substitution product, since in the first case the chlorine found would be too high, and in the second too low. I have substantiated this supposition by again distilling Fraction II*b* to one-half, and analysing it.

Fraction II*b* 1.

0·3245 gram substance produced 0·266 gram AgCl = 20·2 per cent. Cl.

0·3140 gram substance produced 0·6200 gram CO_2 and 0·2005 gram H_2O.

	Calculated for $CH_3{\cdot}CCl : C(C_2H_5){\cdot}COOC_2H_5$.		Found.	
			I.	II.
C_8	96	54·4	—	53·85
H_{13}..........	13	7·36	—	7·09
O_2	32	—	—	—
Cl	35·5	20·11	20·2	—
	176·5			

Although the percentage of chlorine found agrees with the above formula, still the carbon, and especially the hydrogen, are too low. It is, I think, extremely probable that this substance consists mainly of pure ethylic ethylchlorcrotonate, as the evolution of ethyl chloride and the occurrence of phosphorus oxychloride can then be satisfactorily accounted for.

Fraction III.—Analyses have shown this fraction to be a dichloro-substitution product of ethylic diethylacetoacetate.

I. 0·274 gram substance produced 0·297 gram AgCl.

II. 0·3135 „ „ „ 0·5455 gram CO_2 and 0·182 gram H_2O.

The oil was now distilled to one-half, and that remaining in the flask dried and analysed for chlorine. The percentage was found to be nearly the same.

* In these operations a long-necked flask was used, and the tube in connection with the condenser was about $\frac{1}{3}$ in. in diameter.

III. 0·2775 gram substance gave 0·319 gram AgCl.

	Calculated for $CHCl_2 \cdot CO \cdot C(C_2H_5)_2 \cdot COOC_2H_5$.		Found.		
			I.	II.	III.
C_{10}	120	47·05	—	47·4	—
H_{16}	16	6·27	—	6·4	—
O_3	48	—	—	—	—
Cl_2	71	27·84	26·8	—	28·4
	255				

Ethylic diethyldichloracetoacetate is an oily, slightly yellow liquid, having a pleasant odour. It is insoluble in water, but miscible with alcohol and ether, and has at 15° a sp. gr. of 1·155. It cannot be distilled under the ordinary pressure.

Fraction IV.—This liquid, consisting of the last drops which were distilled, appears to contain about 50 per cent. of a trichloro-substitution product of ethylic diethylacetoacetate, the percentage of chlorine in which is 36·8.

0·2115 gram produced 0·2655 gram AgCl = 31·06 per cent. Cl.

II. *Formation of Oxyketones—Action of Sodium Methylate on Ethylic Diethylchloracetoacetate.*

A solution of 4·2 grams of sodium (1 mol.) in 40 grams of methyl alcohol was poured into 40 grams of ethylic diethylmonochloracetoacetate* contained in a flask; a reaction took place at once with considerable elevation of temperature, the liquid becoming brown. It was necessary to place the flask in cold water for a time, but afterwards the mixture was heated on the water-bath, and finally in sealed tubes for three hours at 100°. The contents of the tubes were then distilled to dryness on an oil-bath, and the distillate fractionated. Most of the methyl alcohol was thus separated, and the residue, which boiled from about 80° upwards, was shaken with a saturated solution of calcium chloride several times, and the upper layer separated and submitted to fractional distillation. From this liquid, I succeeded in obtaining two compounds; one boiled at 130—132° and represented the principal part, the other passed over between 185—190° and was obtained only in small quantity.

An analysis of the liquid boiling at 185—190°, which still contained a little chlorine, gave the following numbers:—

* Obtained from 100 grams of diethylacetoacetate and PCl_5. After distilling 1 or 2 c.c. in a current of steam, the remainder was collected until about two-fifths of the whole had passed over.

0·2265 gram substance produced 0·5135 gram CO_2 and 0·1855 gram H_2O.

	Calculated for $C_{11}H_{20}O_4$.		Found.
C_{11}........	132	61·11	61·82
H_{20}	20	9·21	9·09
O_4........	64	29·68	—
	216	100·00	

This result agrees in the main with the composition of ethylic methoxydiethylacetoacetate, $CH_2(OCH_3)·CO·C(C_2H_5)_2·COOC_2H_5$. It is a pleasant smelling, colourless liquid, soluble in alcohol and ether, and heavier than water, in which it is insoluble.

I have not been able to obtain this compound free from chlorine. If an excess of sodium methylate is taken, in order to remove the whole of the chlorine, the substance boiling from 130—132° is chiefly produced.

Analysis of the body boiling from 130—132°:—

I. 0·276 gram substance gave 0·6475 gram CO_2 and 0·268 gram H_2O.

II. 0·2745 gram substance, obtained from a second preparation, gave 0·6465 gram CO_2 and 0·2725 gram H_2O.

III. 0·2465 gram of the same substance gave 0·5820 gram CO_2 and 0·2415 gram H_2O.

IV. 0·320 gram of the portion boiling from 125—130°, which was very little, gave 0·7600 gram CO_2 and 0·317 gram H_2O.

	Calculated for $C_7H_{14}O_2$.		Found. I.	II.	III.	IV.
C_7	84	64·6	64·0	64·2	64·4	64·7
H_{14}	14	10·8	10·78	11·03	10·84	11·0
O_2	32	24·6	—	—	—	—
	130	100·0				

These numbers agree pretty well with each other, and with the formula of an oxyketone, viz., methoxymethyl-ethyl-acetone (*methoxymethyl butyl ketone*), $CH_2(OCH_3)·CO·CH(CH_3)(C_2H_5)$. It might certainly have been expected that a methoxy-*diethyl*-acetone would have been formed, according to the following equations :—

$$CH_2Cl{\cdot}CO{\cdot}CEt_2{\cdot}COOEt + CH_3{\cdot}ONa = CH_2(OCH_3){\cdot}CO{\cdot}CEt_2{\cdot}COOEt + NaCl.$$

$$CH_2(OCH_3){\cdot}CO{\cdot}CEt_2{\cdot}COOEt + H_2O = CH_2(OCH_3){\cdot}CO{\cdot}CHEt_2 + CO_2 + EtOH.$$

But this, according to the analytical results, does not appear to be the case. The place of one ethyl-group has been taken by methyl, and this displacement is probably brought about by the excess of methyl alcohol. The researches of Geuther and Bachmann (*Annalen*, **218**, 49) have already shown that in the case of the ketals (and this oxy-ketone is possibly nearly related to them) a positive organic radicle can be displaced by another *poorer in carbon*, *e.g.*, by the action of methyl alcohol on diethylacetal, methylethylacetal and dimethylacetal are formed.

Methoxymethyl-ethyl-acetone is a mobile, colourless liquid, of sp. gr. 0·855 at 20°, very much resembling acetal. It has a burning taste and a very pleasant odour, and it can be mixed with alcohol and ether, but is insoluble in water. It boils at 130—132°, and the vapour burns with a luminous flame tinged with blue. No compound with sodium hydrogen sulphite could be obtained.

Action of Sodium Methylate on Ethylic Diethyldichloracetoacetate.

A solution of 9·5 grams of sodium (2 mols.) in 70 grams of methyl alcohol was poured into a flask containing 50 grams of pure ethylic diethyldichloracetoacetate, and the mixture treated precisely as before described. In this case also, I finally obtained two liquids boiling at 134—135° and 190—200°; this last portion was very little, and consisted chiefly of ethylic dimethoxydiethylacetoacetate, as the following analysis shows :—

0·211 gram substance gave 0·4445 gram CO_2 and 0·165 gram H_2O.

	Calculated for $C_{12}H_{22}O_5$.		Found.
C_{12}	144	58·53	57·4
H_{22}	22	8·94	8·7
O_5	80	32·53	—
	246	100·00	

I have endeavoured, in vain, to obtain this substance in a purer state; it always contains a little chlorine, and since it is slightly decomposed by distillation, the chlorine compound cannot be got rid of in this way. An excess of sodium methylate causes a further decomposition, as in the case of the monochlorinated derivative.

Ethylic dimethoxydiethylacetoacetate,

$$CH(OCH_3)_2{\cdot}CO{\cdot}CEt_2{\cdot}COOEt,$$

is a pleasant smelling, colourless liquid, heavier than water, in which it is insoluble ; it boils with partial decomposition about 195°.

An analysis of the substance boiling at 134—135° gave the following result :—

I. 0·3235 gram substance gave 0·7335 gram CO_2 and 0·3065 gram H_2O.

II. 0·239 gram substance gave 0·5455 gram CO_2 and 0·225 gram H_2O.

	Calculated for $C_9H_{18}O_3$.		Found. I.	Found. II.
C_9	108	62·06	61·83	62·24
H_{18}	18	10·34	10·52	10·46
O_3	48	27·60	—	—
	174	100·00		

These numbers correspond very closely with the above formula, which represents a *dimethoxy-diethyl-acetone*,

$$CH(OCH_3)_2{\cdot}CO{\cdot}CH(C_2H_5)_2.$$

The following equations explain its formation :—

$$CHCl_2{\cdot}CO{\cdot}CEt_2{\cdot}COOEt + 2CH_3{\cdot}ONa = CH(OCH_3)_2{\cdot}CO{\cdot}CEt_2{\cdot}COOEt.$$

$$CH(OCH_3)_2{\cdot}CO{\cdot}CEt_2{\cdot}COOEt + H_2O = CH(OCH_3)_2{\cdot}CO{\cdot}CHEt_2 + CO_2 + EtOH.$$

It is a colourless, mobile, pleasant smelling liquid, having a burning taste. It boils at 134°, and has a sp. gr. of 0·886 at 15°. It is insoluble in water, but miscible with alcohol and ether in all proportions. Its vapour burns with a luminous flame. No compounds are formed with acetic anhydride or sodium hydrogen sulphite.

The yield of these two methoxyketones is by no means a good one; this is chiefly because a considerable quantity passes over with the methyl alcohol, and cannot be separated by fractional distillation; still, by adding powdered calcium chloride to the methyl alcohol distillate until a syrup is formed, shaking with ether—which dissolves the oxyketones—and then removing the ether on a water-bath at 50°, I have succeeded in recovering a fair amount of these compounds.

I am not aware that a methoxyketone has been previously described, although L. Henry has recently (*Ber.*, **14**, 2272) prepared the

ethyl salt of the alcohol of pyroracemic acid, $CH_3·CO·CH_2·OC_2H_5$, which he obtained from propargyl ether by means of mercuric bromide and water.

Ammonia and Ethylic Diethylacetoacetate.

By the action of concentrated aqueous ammonia on this substance, it was expected that amides would be obtained analogous to those produced from ethylic acetoacetate, at the same time its abnormal reaction with phosphorus pentachloride seemed to predict failure, and this prediction has been verified by experiment. No reaction takes place at 120—130° in sealed tubes, and on heating still higher, finally to 190—200°, the ethylic diethylacetoacetate becomes decomposed, forming ammonium carbonate and diethylacetone boiling at 135—137°.

VIII.—*On the Sugars of Some Cereals and of Germinated Grain.*

By C. O'Sullivan, F.R.S.

In the analyses of the cereals, and of germinated grain hitherto published, if sugar is mentioned as one of the constituents, the particular sugar or sugars have not been specified. Kühneman, *Ber.*, 8, 202, indeed, states that he isolated 0·6 to 1 per cent. sucrose (cane-sugar) from germinated barley; the evidence for the statement, as published, is, however, unsatisfactory and unconvincing. As the question of the presence or absence of a sugar or sugars, and a determination of the particular variety thereof, is of considerable practical importance, I may be permitted to record the results of an investigation undertaken with this object in view.

I shall describe the experiments with barley, as the operations employed in dealing with it answer also for the other cereals, raw and germinated.

The ground grain, when treated with water, yields the sugars to that solvent, but, at the same time, other compounds are dissolved, which render it impossible to bring the solution into such a condition as would admit of its being satisfactorily worked with. The amount of material which it is necessary to take requires the employment of much solvent, so that the washings are very dilute, and the solution cannot be concentrated, unless, indeed, under diminished pressure, without the development of much colour, and the formation of decomposition products. I have, on another occasion, pointed out that

alcohol, sp. gr. 0·90, yields a clean, fairly workable solution, but the amount of mucidin and fibrin dissolved is so great that it is almost impossible to concentrate the extract obtained with it by distillation, because, when the greater part of the alcohol has passed over, the liquid in the distilling flask froths up and is carried over in quantity. Strong spirit, in which the albuminoïds are insoluble, cannot be used with advantage, as the sugars are not very soluble in it. In consequence of these considerations, I found it necessary to proceed as follows.

200 grams finely ground barley (this was a convenient quantity to work with), were introduced into a flask capable of holding 1·5 litres; 200 c.c. of alcohol (sp. gr. 0·9) added, and the mixture allowed to stand for 24 hours. 400 c.c. alcohol, sp. gr. 0·84, were then added, and the whole digested at 40° for four hours. The solution was filtered while still warm, and the filtrate kept by itself to cool; the residue being washed by decantation several times with alcohol, sp. gr. 0·85—0·86. It is well to keep the first 200 or 300 c.c. of washings by themselves, because they, as well as the first filtrate, deposit a considerable quantity of albuminoïd on cooling. When the extract and the first portion of the washings had become clear, after cooling, they were mixed with the final washings and submitted to distillation, 300 or 400 c.c. at a time. Each portion was concentrated to about 50 c.c., and the residues were collected and allowed to cool. Much albuminoïd separated, and after 24 hours the supernatant liquid was bright. This was again decanted into a distilling flask, the insoluble deposit washed with a little water, the washings added to the contents of the flask, and the whole submitted to distillation until the residue was less than 100 c.c. and free from alcohol. This was shaken with a little aluminium hydroxide and filtered; the filtrate with the washings was made up to 100 c.c. As the extraction and the washing had been carefully done, this 100 c.c. contained all the ready formed sugars of the 200 grams barley: the solution was sufficiently bright for optical observations. The sp. gr.* of the solution was found to be 1·02445; it had an optical activity = 10·1 divisions,† in a 200 mm. tube of a Soleil-Scheibler saccharimeter, and 12·159 grams of it reduced 0·1943 gram CuO. 80 c.c. of the solution

* In speaking of specific gravity it will be understood that I mean the weight of the solution compared with the weight of water, the bulks and temperatures being equal, and the weight expressed in the ratio of water = 1. I make the comparison at 15·5°, and this may be indicated sp. gr. $\frac{15\cdot 5^\circ}{15\cdot 5} = 1$.

† In this paper, I employ the divisions of a Soleil-Scheibler instrument to express the optical activity, because they answer the purpose as well as angular values, and the trouble of calculation is thereby avoided. The observations are all made in a 200 mm. tube and at a temperature of 15·5°.

were digested in a flask with 0·03 gram *invertase* for 4 hours at 52—54°;* after cooling, the contents of the flask were made up to the original bulk (80 c.c.) by the addition of a few drops of water, and filtered. The solution was then sufficiently bright for an optical observation. Occasionally, however, the filtrate, obtained in the way indicated, from some material, requires to be treated with a little animal charcoal; in such cases, the least possible quantity should be used. The sp. gr. of the filtered solution was found to have increased to 1·02525, the optical activity to have diminished to − 2·51 divs., and the K to have increased—3·146 grams solution reduced 0·243 gram CuO.

From these data, the K of the original solution was = 0·74 gram dextrose, which was increased to 3·58 grams by the action of invertase; the loss in optical activity on inversion was represented by 12·61 divs. (10·1 + 2·51); and the increase of solid matter, as indicated by the sp. gr., was = 0·21 gram.† The original solution, therefore, contained a substance capable of being acted upon by invertase, yielding thereby a substance of increased reducing power, of diminished optical activity, and of increased sp. gr. These are some of the properties of sucrose; in fact, there is no other known sugar acted upon by invertase in the way described. Let us see how the factors observed agree with those belonging to that sugar—how the increase in reducing power agrees with the diminution in optical activity. The 2·84 grams (3·58 − 0·74) of reduction would be yielded by the inversion of 2·69 grams sucrose, because

105·25 : 100 : : 2·84 : 2·69,

the first term being the amount of invert sugar yielded by 100 grams of cane-sugar. Now 1 gram sucrose in 100 c.c. solution, when acted upon by invertase, loses an optical activity = 5·18 divs., the observed loss was 12·61 divs.; hence, 12·61 ÷ 5·18 = 2·43, the grams of sucrose in the 100 c.c. solution. We thus see that—

the optical activity indicates 2·43 grams sucrose, and
the reduction „ 2·69 „ sucrose.

Further, 2·69 grams sucrose, on being inverted, take up 0·15 gram water; the observed increase in sp. gr. indicates 0·21 gram, including the invertase. In this experiment the agreement between the sucrose, calculated from the optical activity and the reduction, is not as close as usual; in another experiment

the optical activity yielded 2·79 grams sucrose, and
the reduction „ 2·77 „ sucrose;

* If sulphuric acid were employed, it would act not only upon the sucrose, but also upon maltose and dextrose, should they be present.

† Part of this is, no doubt, due to concentration during filtration.

and the results of very many determinations lie between these two extremes. Hence the evidence for the presence of sucrose is as conclusive as need be desired.

Having obtained this evidence, we may turn to an examination of the reducing power in the original 100 c.c. solution, and see if we can determine to what sugar or sugars it was due.

It may have been due to inverted sucrose; if so, the optical activity of the amount of reduction, taken as invert sugar, plus the optical activity of the sucrose found, should be equal to the optical activity observed. The original reduction corresponds to 0·74 gram invert sugar, and we may take the sucrose at 2·69 grams; now 1 gram sucrose in 100 c.c. solution is equal to 3·84 divs., and 1 gram invert sugar to $-$ 1·23 divs.; hence $2·69 \times 3·84 = 10·33$ less $0·74 \times 1·23 = 0·91 = 9·42$, the number of divisions corresponding to such a mixture; the activity observed was 10·1 divs. These numbers do not agree sufficiently closely to give any support to the supposition, and, even if the approximation were closer, the evidence for the inference would be far from conclusive. Of course, if the quantity of sucrose indicated by the optical activity were taken for the purpose of the calculation, the difference between the observed and calculated numbers would be greater.

A mixture of lævulose and dextrose could be worked out to fit in with the observed optical activity, but this would be in no way satisfactory; I, therefore, tried by other means to obtain evidence of the character of the sugar.

66·939 grams of the inverted solution were sterilised by boiling and cooled; 0·4 gram pressed yeast was added to them, and fermentation allowed to take place, first at the ordinary temperature, and then at 20—22°. The apparatus in which this operation was conducted consisted of a flask capable of holding 120 c.c., in which was the fermenting liquid, and two small wash-bottles, through a few c.c. of water in each of which the carbon dioxide evolved was made to pass. At the end of 10 days, when all action had ceased, the fermented liquid was transferred to a distilling flask, the first rinsings being made with the water of the wash-bottles, and further with a few c.c. water, care being taken that the liquid and washings did not much exceed 100 c.c. The distillate was collected in a 100 c.c. vessel, as is done in the usual method of determining original gravities. When nearly 100 c.c. had passed over the operation was stopped, and the distillate made up at 15·5° to 100 c.c. Of this the sp. gr. was found to be 0·99772, which, according to Fownes' tables, is equal to 1·22 grams absolute alcohol in the 100 c.c. Now as only 66·939 grams original solution, sp. gr. 1·02525, were taken, we arrive at the quantity of alcohol derivable from the whole 100 c.c. by the proportion —

66·94 : 102·53 : : 1·22 grams : 1·87 grams;

that is, the original 100 c.c. solution would have yielded 1·87 grams absolute alcohol. According to the best available determinations (Pasteur, *Ann. Chim. Phys.*, **58**, 323), 100 grams of a $C_6H_{12}O_6$ sugar yield 48·5 grams alcohol; the 1·87 gram is, therefore, the product of 3·86 grams sugar, for—

$$48{\cdot}5 : 100 :: 1{\cdot}87 : 3{\cdot}86.$$

The reducing power in the inverted solution was only = 3·58 grams of dextrose; hence, we have here an indication that a sugar with a less reducing power than invert sugar, or one with no reducing power at all, had fermented.

Let us now compare these numbers with the amount of solid matter that disappeared from the solution during fermentation. The contents of the distilling flask were transferred to a 100 c.c. measure, and with the washings, were made up to the 100 c.c. mark at 15·5°. The sp. gr. was found to be, with the yeast in, 1·00676, and, after the yeast was separated by filtration, 1·00620. The 0·4 gram yeast originally added contained 0·13 gram solid matter, whereas the presence of the yeast in the fermented liquid was indicated by a sp. gr. of 1·00056 = about 0·14 gram; consequently, the yeast may be considered to have done its work without having taken anything from, or yielding anything to the solution. Had the whole 100 c.c. been taken, the sp. gr. of the residue would have been 1·00948, because—

$$66{\cdot}94 : 102{\cdot}53 :: 620 : 948;$$

hence, 1·02525 − 0·00948 = 1·01577, the sp. gr. in 100 c.c. of the matter fermented. If we take 1·00385 as representing the gravity of 1 gram sugar in 100 c.c. solution, the sp. gr. of the matter fermented indicates 4·09 grams, and this without taking into account the glycerin, succinic acid, &c., produced. We have then the following numbers for the sugars in the inverted solution:—

3·58	grams	from	reduction,
3·87	,,	,,	the alcohol on fermentation, and
4·09	,,	,,	the gravity lost on fermentation.

The numbers calculated from the alcohol and from the gravity lost on fermentation should agree better than they do in this case, and I may say, they usually do; but these results afford a clear indication of the facts generally observed. Without giving preference to any one number, we may, for our purpose, take that derived from the alcohol as the amount of sugar that had fermented. When we compare this with the amount of sugar represented by the reducing power, we observe that at least 0·29 gram (3·87 − 3·58) of matter which had no

reducing power fermented. This is a property of maltose, but the body may be any non-reducing sugar not acted upon by invertase.

Before we enter, however, into a consideration of this part of the subject, I must mention that the unfermented residue had no optical activity, and that 25 c.c. of it, boiled with 10 c.c. Fehling's solution properly diluted, gave no trace of reduction even after 15 minutes' boiling; a slight precipitate did form, it is true, but this was flocculent and white; hence, all the sugars had fermented. This result is not always obtainable; the residue very frequently exhibits an optical activity, and possesses a reducing power. Sometimes, the relation of the reducing power to the optical activity is such as to indicate the presence of maltose, but, as a rule, the relation holds good for no known sugar, and the optical activity is high for the reduction, higher than would be indicated by dextrose, but no definite factors can be arrived at, the quantities are too small. The residual optical activity being a + quantity, the sugar cannot be lævulose, and it must be less fermentable than that sugar; or it would not have been left behind whilst the invert sugar disappeared.

Now, to return to the matter fermented: it seems at first sight as if the 0·29 gram of non-reducing power, described above as disappearing during fermentation, might be due to the presence and fermentation of 0·77 gram maltose (37·5, the non-reducing power of maltose : 0·29 : : 100 : 0·77), but when we consider that the optical activity due to the sucrose is + 10·33 divs., whilst the original activity was only = 10·1, we see that the sugars other than sucrose must have a minus power = − 0·23, and, therefore, this could not under any circumstances be due to maltose alone, and probably not to any mixture of maltose with other sugars. If it were not for the disappearance of this non-reducing matter during fermentation, it would appear probable that the original reducing power, judging from the optical activity, is due to dextrose and lævulose, the former being in excess.

I may state that when barley has been extracted with alcohol as described, if the residue is treated with water, the aqueous solution concentrated, and the amylans and other substances precipitated by alcohol, sp. gr. 0·84, the alcoholic supernatant liquid contains no optically active or reducing substance. This I proved by distilling off the alcohol, and concentrating the residue to a small bulk. All the sugars of barley can, therefore, be dissolved by careful treatment with alcohol as described above.

Such are the general indications regarding the sugars in barley. The results of the examination of at least 20 varieties may be summarised as follows:—

1st. The diminution in optical activity and the increase in reducing

power, produced by the action of invertase, agree well with the factors of sucrose, and the numbers obtained show that barley contains between 0·8 and 1·6 per cent. of that body.

2nd. There is a variable quantity of a sugar or sugars present which reduce less than dextrose, and the optical activity of which is always a minus quantity, but I have not been able to establish any satisfactory constant relation between the optical activity and K.

3rd. Frequently the solution containing the sugars does not completely ferment; when this is the case the residue has a positive optical activity and a K which are variable, and cannot be referred to any known sugar. The substance is less fermentable than lævulose.

Wheat, treated in the same way, yields not more than 0·5 per cent. sucrose, but there are indications of a moderately high lævorotary, non-reducing, fermentable sugar of which I hope to be able to say something at a future time.

In dealing with germinated barley (malt), I found 100 grams sufficient for the purpose, but as it is well to have at least 125 c.c. of solution, I employ 125 grams substance.

125 grams malt, finely ground, were digested at 40° with 500 c.c. alcohol sp. gr. 0·9 for six hours; to this 700 c.c. of alcohol, sp. gr. 0·84, were added, and the mixture allowed to stand for 24 hours. The clear supernatant liquid was decanted through a filter, and the residue washed gradually with 400 to 500 c.c. of alcohol of the last-named strength. The filtrate was then treated in the same way as is described in the case of barley, and 125 c.c. of fairly colourless, bright, aqueous solution obtained. The sp. gr. of this solution was 1·4890, and its optical activity = 35·5 divs. In determining the reduction—

1st Exp. 2·793 grams solution gave 0 207 gram CuO.
2nd Exp. 2·920 ,, ,, ,, 0·217 ,, CuO.

These numbers correspond to—

1st Exp. 3·52 grams dextrose in 100 c.c. solution, and
2nd Exp. 3·53 ,, ,, ,, solution.

To 100 c.c. of the solution, 0·06 gram invertase was added, and the whole digested at 50—53° for four hours. This was sufficient to completely invert any sucrose that may have been present. The solution was cooled to 15·5°, and then made up with a few drops of water to 100 c.c. The sp. gr. of this solution was 1·05020, and its optical activity = 11·2 divs.:—

1st Exp. 1·322 grams of it gave 0·239 gram CuO, and
2nd Exp. 1·124 ,, ,, 0·204 ,, CuO.

These numbers correspond to—

1st Exp. 8·61 grams dextrose in 100 c.c. solution, and
2nd Exp. 8·64 „ „ „ solution.

The increase in reduction is, therefore, equal to 5·11 (8·64 − 3·53 = 5·11) grams dextrose or invert sugar, corresponding to 4·85 grams $\left(\frac{5·11}{1·0526} = 4·85\right)$ sucrose.

The optical activity in the original solution was 35·5 divs.; after inversion, it was 11·2 divs.; there was consequently a loss of 24·3 divs.; a loss of 5·18 divs. corresponds to 1 gram sucrose in 100 c.c., and $\frac{24·3}{5·18} = 4·69$, the number of grams sucrose indicated by the decrease in optical activity.

We have then, in the 100 c.c. solution, 4·85 grams sucrose indicated by the increase of reduction, and 4·69 grams sucrose indicated by the decrease in optical activity.

These numbers, it will be observed, are percentages on the malt taken.

In order to obtain some knowledge of the character of the reducing bodies in the original solution, the inverted solution was submitted to fermentation. Before examining the results of this experiment, it may be as well to consider with what compounds we are likely to have to deal.

We may take it that the original solution contained 4·7 grams sucrose in 100 c.c.; the optical activity due to this is 18·05 divs. (4·7 × 3·84); hence, 35·5 − 18·05 = 17·45 divs., are due to the sugars represented by the 3·53 grams of reduction. If the reduction be taken as dextrose, the optical activity is too high, if as maltose, too low; a mixture of maltose and dextrose could be calculated to agree with it, and one in which lævulose was also present could be made to fit in, but as we have no evidence of the presence of either sugar at present, we must turn to the fermentation experiment to throw some light on the subject.

102·4 grams of the inverted solution were sterilised and submitted to fermentation with 0·5 gram pressed yeast, the usual precautions being taken to make the carbon dioxide evolved pass through two wash-bottles containing a little water. Towards the end, it was necessary to add 0·002 to 0·003 gram active diastase to ensure the complete fermentation of the optically active and reducing bodies.

The fermentation finished, the solution yielded on distillation—

100 c.c. alcohol, sp. gr. 0·99193, and
100 c.c. residue, sp. gr. 1·01473 with yeast in, and
sp. gr. 1·01392 „ out.

The clear filtered residue was optically inactive and had no reducing power.

The sp. gr. of the distillate indicates 4·50 grams alcohol in the 100 c.c., and if it be admitted that this is derived from a $C_6H_{12}O_6$ sugar, we get from the proportion

$$48{\cdot}5 : 100 : : 4{\cdot}5 : 9{\cdot}28$$

the number of grams of sugar whence it was derived. Now as only 102·4 grams of the original solution were employed, the proportion

$$102{\cdot}4 : 105{\cdot}02 : : 9{\cdot}28 : 9{\cdot}51$$

gives the grams fermentable in that solution. On the other hand the total reduction was equal only to 8·64 grams dextrose; hence, it would appear from this, that 0·87 gram of matter not indicated by reducing power fermented, but as we have no evidence that all the alcohol was derived from a $C_6H_{12}O_6$ sugar, the factor is not of so much value as is desirable. Let us see what can be made of the difference between the original sp. gr. of the solution and that of the residue.

As pointed out above, the 102·4 grams solution gave 100 c.c. residue, sp. gr. 1·01473 with yeast in, and 1·01392 after the yeast was separated by filtration. The amount of yeast in the residue was represented, therefore, by 100 c.c., sp. gr. 1·00081. 4·264 grams of the pressed yeast employed, suspended in 100 c.c. water, gave a sp. gr. = 1·00466; the 0·5 gram used would, therefore, give a sp. gr. = 1·00054, thus leaving a quantity of matter represented by 100 c.c. solution, sp. gr. 1·00027 (0·00081 − 0·00054) : this does not amount to more than 0·07 gram, and as we do not know at present whence it is derived, we may neglect it. The unfermented residue that was left on the fermentation of the 102·4 grams inverted solution amounted to 100 c.c. of sp. gr. 1·01392, which, calculated out in the same way as was the barley residue, gives the matter disappearing during fermentation as 9·33 grams; but this figure can, as was before shown, only be taken as an approximation. The number calculated from the alcohol is 9·51, but this may be too high, a $C_{12}H_{22}O_{11}$ sugar may have yielded a portion of it, whereas that derived from the gravity must be too low, as the glycerin, succinic acid, &c., were not allowed for. If, therefore, the mean of the numbers be taken, we cannot be far from the truth; in this way we arrive at 9·42 grams as the amount of matter fermented.

The reduction before fermentation represented 8·64 grams sugar, and as 9·42 grams fermented, 0·78 gram of matter without reducing power must have disappeared. If this be attributed to maltose, we have 2·08 grams of that compound, because

$$37{\cdot}5 : 100 : : 0{\cdot}78 : 2{\cdot}08\,;$$

and 9·42 − 2·08 = 7·34 grams other sugars. 4·7 grams sucrose yield 4·94 grams invert sugar (reduction), and 2·08 grams maltose give 1·30 grams reduction; consequently, the original solution contained 2·40 grams of other reducing sugars—

$$8{\cdot}64 - (4{\cdot}94 + 1{\cdot}30) = 2{\cdot}40.$$

Admitting the quantity of sucrose and maltose to be correct, let us see what optical activity will belong to these sugars.

Sucrose	4·7 × 3·84 =	18·05 divs.
Maltose	2·08 × 8·02 =	16·68 „
	Total	34·73 „

The observed activity was 35·5 divs., thus leaving a dextro-power = 0·77 divs. for the 2·4 grams sugar. These may be lævulose and dextrose, the latter being in excess. The quantity of each, in 100 c.c., may be calculated thus:—

$$\frac{5{\cdot}52 \times 2{\cdot}4 + 0{\cdot}77}{2{\cdot}96 + 5{\cdot}52} = 1{\cdot}65 \text{ gram dextrose,}$$

and 2·4 − 1·65 = 0·75 gram lævulose; − 5·52 and 2·96 being the number of divisions due to 1 gram lævulose and 1 gram dextrose respectively in 100 c.c. solution; 2·4 the total sugar in grams, and 0·77 the optical activity in divisions due to them.

From these data, the malt employed contained—

Sucrose...........	4·70	per cent.
Maltose...........	2·08	„
Dextrose	1·65	„
Lævulose	0·75	„
Total sugars......	9·18	„
Add	0·24	for the hydration of sucrose,
and we get	9·42	the amount of matter that

disappeared during fermentation.

Results similar to these have been obtained for all the malts worked with.

I have tried to give, as clearly as possible, the evidence for the presence of each sugar; that for the sucrose leaves little to be desired, it is satisfactory; with regard to the maltose the evidence is not so convincing, for, although a certain quantity of matter without reducing power disappears during fermentation, and the solution has a sufficient optical activity to admit of the presence of the amount of maltose calculated therefrom, as we have no means of checking one result by the other, we cannot say that the observed facts are due

absolutely to maltose; of that for the lævulose and dextrose all that can be said is, that there is a reducing power with which certain mixtures of them correspond, and, that when the cane-sugar is low in a malt, its place is taken by a reducing power and optical activity which can be referred to lævulose and dextrose.

I shall, however, show that it is not difficult to strengthen the evidence for the presence of maltose. In nearly all cases, in the fermentation experiments, unless a little active diastase had been added to the solution, it was, after the fermentation had ceased, optically active and reduced copper solution, the optical activity being, as a rule, but not always, equal to that of maltose calculated from the reduction. This is usually the case when the fermented solution gives a reduction* equal to from 0·6 to 0·8 gram dextrose, corresponding to 0·9 to 1·1 of maltose in 100 c.c. Sometimes, indeed, the optical activity is greater than the maltose calculated from the reduction; this may be attributed to a little dextrin or malto-dextrin, and it very probably is due to one or both, but I have no farther evidence to prove it. I met with the indication only in a few malts.

Before summing up the results, I should state that it is very difficult to free malts from sugars by treatment with alcohol; indeed, although I have made at least 20 estimations, I have only succeeded in a few cases in obtaining a residue perfectly free from sugar. To determine the point, the residue was treated with water at 40°, the extract evaporated to a small bulk, which is, in this case, easily accomplished without the development of much colour, and 40 to 50 c.c. hot alcohol (0·85) added; this throws down much flocculent matter, and the clear supernatant liquid contains the sugar. This is usually maltose, as invertase produces no change, and the reducing power and optical activity corresponds to maltose. In this way, I have found as much as 0·7 gram sugar left behind on treating 100 grams malt. This may be due to the action of water and a little diastase on the broken starch granules, but I think it is hardly so, as very little, if any, of the transforming agent can be present.

The chief results obtained from the analyses of over 20 samples of malt, from various sources, by the method described, may be summarised as follows :—

* The estimation of the reduction in the fermented solution leaves much to be desired, in consequence of the precipitation of other matter with the copper suboxide. When sufficient reduction is given by 12 to 15 c.c. of the solution, and these are heated to boiling, and added to the boiling dilute copper solution gradually, the precipitate represents the reduction fairly accurately, but when the reducing power is low, and 25 to 30 c.c. of the fermented solution have to be taken, the precipitate is decidedly impure; it blackens on drying, and, on ignition, burns like tinder.

1st. Malts contain from—

2·8 to 6·0	per cent.	sucrose,
1·3 to 5·0	,,	maltose,
1·5 to 3·0	,,	dextrose, and
0·7 to 1·5	,,	lævulose.

This does not mean that any variety contains only the maximum or the minimum of all the sugars, but that the numbers given were those observed in individual cases.

2nd. As a general rule, the sucrose and maltose are high in highly germinated grain, and, when the sucrose is low in such grain, its place is taken by the products of its inversion, lævulose and dextrose.

3rd. The numbers given as the results of the above described experiment may be taken as fairly typical.

Without going into details, I may say that germinated wheat yields similar results.

That some idea may be conveyed of the changes that take place in the sugars during germination, I give the results of the analyses of two barleys before and after germination, calculated per cent. on the dry matter of the barley, the yield of dry malt being known.

Sugars.	No. 1 barley.		No. 2 barley.	
	Before germination.	After germination.	Before germination.	After germination.
Sucrose	0·9	4·5	1·39	4·5
Maltose	} 1·1*	1·2	} 0·62*	1·98
Dextrose		3·1		1·57
Lævulose		0·2		0·71

From this, it is clear that during germination sucrose increases largely, and that there is a decided production of maltose, dextrose, and lævulose. The high dextrose in No. 1 germinated barley is frequently observed, but then, as in this case, the maltose is low, the fact pointing apparently to a conversion of that body.

Starch disappears to a considerable extent during germination; from it the maltose is most probably derived. The source of the sucrose, and of the products of its inversion, is not so easily indicated.

I need hardly point out that sucrose can be easily detected in unfermented malt-wort by the loss of optical activity on addition of

* Sugars other than sucrose, by fermentation experiment.

invertase. This inversion also takes place immediately on the addition of yeast, or in a short time if the wort be kept after exposure to the air, doubtless from the growth of fortuitous yeast. In a wort sp. gr. 1·065, a diminution of as few as 5 and as many as 10 divs., corresponding respectively to 5·7 and 11·4 per cent. sucrose on the wort matter, have been observed on digestion at 50—52° with invertase.

In conclusion, I may say that I have simply given the evidence from which my inferences are drawn; this evidence must be taken for what it appears to be worth; for myself, I shall not be satisfied until each individual sugar is separated, crystallised, and examined by itself. Further, I have as briefly as possible indicated how the data were obtained; if I were to give all the analytical numbers upon which the inferences are based, I should have to occupy much more space than the facts outside the inferences are worth.

My thanks are due to my brother James, and to my friend Mr. F. W. Tompson, for much assistance in doing this work.

IX.—*On the Presence of "Raffinose" in Barley.*

By C. O'Sullivan, F.R.S.

In the preceding communication, I pointed out that, although the evidence for the presence of certain sugars in barley was moderately conclusive, we could not be absolutely satisfied until each sugar was isolated and examined by itself. So convinced was I of the truth of this proposition that eight or ten years ago, early in my investigation on the sugars of the cereals, I made an attempt to crystallise them. With that object in view, 2 kilos. of ground barley were extracted with alcohol in the same way as is described for the 200 grams in the last paper. The solution, freed from alcohol, was evaporated to a syrup, which was dissolved in the least possible quantity of boiling alcohol, sp. gr. 0·83. This solution, on cooling, deposited a syrup which was again dissolved in just sufficient alcohol to hold it in solution when cold; a little ether was then added to produce a slight turbidity, and the whole put aside to crystallise. In a short time, cauliflower-like segregations began to form, and after a few months they ceased to increase. These were collected, washed with strong alcohol, and put aside labelled "Sucrose (cane-sugar) from barley," for no other reason than that they appeared under pretty much the same conditions as those under which Kühneman (*Ber.*, 8, 202) said he isolated cane-

sugar from malt. The quantity I obtained was not large; it did not amount to more than 1·4 grams, or about 0·07 per cent. of the barley employed. Although this was amply sufficient to determine whether it was sucrose or not, so certain was I that it was, its crystalline appearance notwithstanding, that I did not think it necessary to examine it.

Working with the barley of the season 1878, I believe, in the same way, I obtained 4·55 grams of the cauliflower-like segregations from 5 kilos. material. This too I put aside, labelled "Cane-sugar from barley."

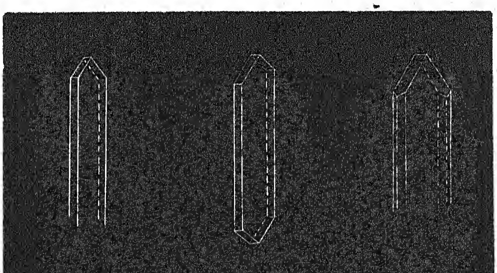
Recently, while arranging the material for the preceding paper, I thought it desirable to examine more closely the two preparations described above. If they were sucrose, I had no doubt I could, by recrystallisation, obtain recognisable crystals of that substance. Before dissolving them, I examined a little of each preparation under the microscope; I found the crystals were elongated, flattened prisms terminated by a dome parallel to the shorter axis, the groups or segregations consisting of the crystals radiating from a centre. Both samples were alike, hence I had undoubtedly to do with a substance altogether different in crystalline form from sucrose. I proceeded to examine the preparations farther.

A determination of the optical activity of the dry matter in the one gave $[\alpha]_j = 125°$, and in the other $[\alpha]_j = 114°$. Both preparations were impure, for each contained a considerable quantity of ash, but it was evident that I had the same substance to deal with.

I dissolved them together in a little water, filtered from some insoluble matter, and added strong alcohol until a precipitate began to appear. This solution, on standing, was filled with radiating groups of beautiful silky crystals, which were collected, and washed with alcohol so regulated in strength as to produce no turbidity in the mother-liquid, the sugar being precipitated as a syrup on adding strong alcohol to the concentrated solution.

The crystals are well-defined, flat, probably rhombic prisms.

FIG. 1. FIG. 2. FIG. 3.



terminated by a brachydome. Figs. 1, 2, and 3 give a fair idea of their shape.

A second crop of crystals was obtained by concentrating the mother-liquor to a syrup, and again adding a little strong alcohol.

On determining the optical activity of these, I found the results did not quite agree; the first crop gave $[\alpha]_j = 129{\cdot}8^\circ$ ($c = 4{\cdot}142$), and the second $[\alpha]_j = 132^\circ$ ($c = 2{\cdot}392$); both still contained ash. As, however, the optical activity was so near, and the quantity of substance at my disposal so small, I mixed the two specimens, and submitted the mixture to recrystallisation.

A first and second crop of crystals were obtained as in the first instance. I now found that both preparations had practically the same optical activity, viz., for the substance dried in a vacuum over sulphuric acid and then in dry air at 100° until the weight was constant, $[\alpha]_j = 134$—135° ($c = 4$ to 5); hence, I concluded I had purified the substance.

1st Exp.—0·992 gram of the crystals, first allowed to remain in dry air until the weight became constant, lost in a vacuum over sulphuric acid 0·142, and then, in dry air at 100°, a farther 0·008 gram, making a total loss of 0·150 gram.

2nd Exp.—2·061 grams, dried in the same way, lost a total of 0·312 gram.

These results indicate—

1st Exp.	15·12 per cent.	water.
2nd Exp.	15·14 ,,	,,

Submitted to combustion in a stream of oxygen, 0·3148 gram dry substance gave—

$$CO_2 = 0{\cdot}4893 \text{ gram, and } H_2O = 0{\cdot}1823;$$

0·0020 gram ash was left in the boat; this was chiefly potassium carbonate.

The numbers give—

		Theory for $C_9H_{16}O_8$.
Carbon......	42·66 per cent.	42·85 per cent.
Hydrogen ...	6·47 ,,	6·35 ,,

These percentages are sufficient to indicate the empirical formula of the body in the dry state, and, from the amount of water lost by the crystals, we get the formula—

$$C_9H_{16}O_8, 2\tfrac{1}{2}H_2O,$$

or by doubling it to eliminate the $\frac{1}{2}$ mol. H_2O,

$$C_{18}H_{32}O_{16}, 5H_2O,$$

which probably represents the molecular formula of the substance.

An aqueous solution containing 1 gram dry substance in 100 c.c. had a sp. gr. 1·003965; this shows conclusively that the substance as burned did not contain any water of crystallisation.

The dry sugar absorbs water from the atmosphere and becomes a glassy mass.

2·227 grams dry substance in 50 c.c. solution gave an optical activity = 31·4 divisions of Soleil-Scheibler's instrument; from this, the specific rotary power for the dry sugar is $[\alpha]_j = +135·3°$.

It does not reduce copper solution; 0·1 gram boiled for 25 minutes with 25 c.c. Fehling's solution, properly diluted, yielded only a trace of copper suboxide.

Invertase appears to act upon it, but very slowly: to 25 c.c. of a solution possessing an optical activity = 28·2 divs., 0·015 gram invertase was added, and the mixture digested at 50—52° for three hours; the optical activity of the cooled solution was = 25 divs. A little more invertase was added, and the digestion continued for another three hours; the activity had then fallen to 21 divs. This was a slow process, but does not leave a doubt that invertase has an invertive action. Had sucrose, in the same quantity, been in the solution, it would have been all inverted in the first three hours. A one per cent. solution of sulphuric acid at 100° reduced the optical activity, in one hour, from 28 divs. to 10 divs. In this case, the products of inversion had a sp. rt. pr. $[\alpha]_j = 43·5°$, and a K = 80·8. The amount of material at my disposal did not warrant farther experiments in this direction, so I did not continue then.

Treated with 4 parts nitric acid and 1 part water, it yielded a little less than 30 per cent. on dry substance of an insoluble acid, which, from its general behaviour and appearance under the microscope, is mucic acid. The filtrate from this acid, neutralised with ammonia and acidified with acetic acid, yielded a precipitate of calcium oxalate on the addition of calcium chloride. From these facts, it is highly probable that galactose is one of the products of inversion, and, from the composition, that two other sugars are produced. These must be saccharic and oxalic acid yielding sugars.

The sugar is fermented by ordinary yeast.

I had worked with this sugar some time under the name of "*cerealose*," but the recent papers of Scheibler (*Ber.*, **18**, 1779) and Tollen (*Ber.*, **18**, 2611) leave no doubt on my mind, that it is the "*raffinose*" of Loiseau (*Compt. rend.*, **82**, 1058). Whether the sugar is Berthelot's mellitose as Tollens says raffinose is, I am not prepared to say.

Scheibler can say whether my description of the crystals agrees with his observations. My analytical numbers agree well with his, for, although he burned the crystals, and I the dry substance, the

results obtained lead to the same formula. The optical activity observed by me, sp. rt. pr. $[\alpha]_j = 135 \cdot 3°$, agrees with the numbers obtained by Scheibler and Tollens, $[\alpha]_D = 104°$; $[\alpha]_j = 114 \cdot 7°$; they evidently, in this case also, have made the calculation for the crystals, I for the dry substance: 114·7° for $C_{18}H_{32}O_{16},5H_2O$, is equal to 135·1° for $C_{18}H_{32}O_{16}$. The sp. gr. of a solution containing 1 gram in 100 c.c. is higher than that given by Tollens; his figures (*Ber.*, **18**, 2616) leading to a true sp. gr. 1·003712 for such a solution, my figure is 1·003956. The yield of mucic acid is practically the same as observed by Berthelot, Scheibler, and Tollens; my number is, however, a little higher than that published by Scheibler, 30 per cent. against 26·7, but I cannot say with the quantity I had to work with that my experiment can lay much claim to absolute accuracy. My observations on the products of inversion do not quite agree with those published by Tollens. He says galactose, dextrose, and lævulose are the products. I found, for the products of the action of sulphuric acid, $[\alpha]_j = 43 \cdot 5°$, and K = ·81; now, if we suppose that the remaining 19 non-K was unaltered sugar, and the 81 composed of equal parts of galactose, dextrose, and lævulose, we get a mixture the optical activity of which works out $[\alpha]_j = 36 \cdot 1°$, a figure sufficiently removed from 43·5° to throw some doubt on the supposition; however, as I have not sufficient substance to settle the point at present, I must leave it.

These facts, then, leave no doubt that I have been dealing with the "raffinose" of Loiseau, which Tollens says is Berthelot's mellitose; the source whence I isolated it seems to me of sufficient interest to record.

X.—*The decomposition and genesis of hydrocarbons at high temperatures.* I. *The products of the manufacture of gas from petroleum.*

By Henry E. Armstrong and A. K. Miller.

1. A preliminary account of our work was given to the Society in June of last year (*Chem. News*, **49**, 285), a somewhat lengthy description of the manufacture of gas from oil, as practised in this country, having been previously communicated by Dr. Armstrong to the Society of Chemical Industry in a paper read before their London Section in April, and printed in their Journal for September, 1884 (pp. 462—468).

2. The investigation was commenced several years ago, and was

carried on almost uninterruptedly during 1884 and the first half of 1885, but the products are so numerous and their separation and identification is attended with such difficulty, that the progress made is far from satisfactory. Nevertheless, a stage has been reached at which it appears desirable to record the results, as they are in part highly suggestive and will lead to new inquiries being undertaken; besides which the methods at our disposal are scarcely sufficient to enable us to unravel the very tangled skein which the investigation presents. An abstract of the present paper is given in the number of the *Abstracts of the Proceedings of the Chemical Society* for June 18th, 1885.

3. The products of the manufacture of oil-gas are historically of great interest, as their examination led Faraday, in 1825, to his momentous discovery of "Bicarburet of Hydrogen," now known as benzene.* Another new compound described in the same paper was obtained from the most volatile portion of the condensed liquor from the oil-gas receivers. According to Faraday's analysis, it contained carbon and hydrogen in the same proportions as olefiant gas, but was of double the density. This is the composition of *butylene*, the discovery of which has therefore always been attributed to Faraday; we shall have occasion later on to consider whether the evidence he adduces is sufficient to warrant this conclusion.

Faraday's memoir affords a considerable amount of information which we think justifies the inference that the oil-gas of the present day differs but little from that then made, although the oils now used are derived from shale and petroleum and it was then customary to use fish or vegetable oil.

4. We have not been able to ascertain that any attempt has been made to add to our knowledge of the chemistry of the subject since Faraday's investigation was published, notwithstanding the attention paid within recent years to the manufacture of oil-gas, excepting that Greville Williams appears to have commenced the examination of the bye-products of its manufacture not long after Dr. Armstrong had begun to study them (*Chem. News*, 1884, p. 197; see also *Jour. Soc. Chem. Ind.*, 1884, p. 462).

5. In describing our work we propose to disregard the order in which the various constituents were separated or identified; our main object being to throw light on the nature of the changes resulting from the decomposition of petroleum hydrocarbons at high temperatures, it will be desirable to give a connected account of the observations relating to each of the series of hydrocarbons which occur in one or other of the products examined, viz., the compressed gas itself;

* "On new compounds of carbon and hydrogen, and on certain other products obtained during the decomposition of oil by heat:" a paper read June 16th, 1825, by M. Faraday, F.R.S., &c., *Phil. Trans.*, 1825, 440—466.

the liquid deposited during compression of the gas, either in a chamber attached to the compressing pump or in the reservoir in which the gas is stored; and the tar which is deposited from the crude gas prior to compression. In this paper, however, we shall deal only with that portion of the gas which is absorbed by bromine and with the steam-distillable portion of the tar.

I. *Benzenoid hydrocarbons.*

6. The liquid deposited during compression of the gas is wholly volatile in steam when recently obtained, and consists of hydrocarbons capable of being polymerised by sulphuric acid, benzenes and a relatively very small proportion of hydrocarbons unattackable by sulphuric acid; the last-mentioned constituents are present in larger quantity in the steam distillate from the tar.

7. On mixing either liquid with moderately dilute sulphuric acid (2 vols. acid 1 vol. water) much heat is developed, and by its action the unsaturated hydrocarbons are for the most part converted into compounds which are not distillable in steam; in order to effect as complete a conversion as possible, it is desirable when the action appears to be at an end to separate the acid from the oil and to treat the latter with stronger acid—4 : 1. In dealing with small quantities a glass stoppered bottle is used; but for large quantities it is well to use a copper can with a tightly fitting metal plug: there is then no danger of the vessel bursting, and it is much easier to quickly cool the mixture. The acid should be added in small quantity at first, and care should be taken in agitating; in working with large quantities it is desirable to steam-distil as soon as the treatment with 2 : 1 acid is at an end, and to well mix the distillate with the stronger acid, as owing to the viscid character of the product it becomes very difficult to complete the conversion of the unsaturated hydrocarbons into polymerides.

The steam distillate finally obtained has a peculiar characteristic unpleasant odour, due apparently to the presence of volatile products of the action of the acid.

8. A large quantity of benzene may be directly crystallised out from the product so obtained from the liquid deposited from the gas during compression in the manner first described by Faraday and made popular many years later by Mansfield. We have employed a very simple apparatus for the purpose, consisting of a cylindrical vessel, closed only at the bottom, 12 inches high and 4·5 inches in diameter, made of brass $\frac{1}{16}$ of an inch thick; into this fits fairly closely a similar cylinder, the bottom of which has numerous fine holes bored through it. The larger cylinder is placed in a wooden pail or tub, surrounded

with a good freezing mixture, and the hydrocarbon is then poured into it; the walls of the cylinder soon become coated with crystals, which are detached by means of a stout metal rod, and this is frequently used in stirring the contents of the cylinder. When crystallisation is complete, the smaller cylinder is pushed down upon the crystalline pulp, the pail is placed between the jaws of an ordinary long carpenters' cramp, a block of wood is placed across the mouth of the inner cylinder, and pressure is gradually applied by turning the screw of the cramp. The expressed liquid is syphoned off as it rises into the interior of the cylinder. Pressure having been applied to a sufficient extent and during a sufficient length of time, the screw is released, the ram withdrawn, the cylinder lifted out of the freezing mixture, and the small amount of liquid floating on the solid cake is poured out; the benzene is then caused to melt by lowering into it a tube fitted up after the manner of a wash-bottle, through which steam is being passed.

If the mother-liquor from the crystals be fractionally distilled, and the portions boiling near to 80° be then treated as above described, a further considerable quantity of crystalline benzene may easily be obtained.

In like manner the lowest fractions of the product obtained on agitating the steam distillate from the tar with acid, &c., also yield benzene.

The benzene thus separated is by no means pure, and should be treated with alkaline permanganate, bromine, or sulphuric acid, fractionally distilled, and again crystallised.

9. As much of the benzene as possible having been removed, the residue is now extracted with hot concentrated sulphuric acid, and the benzenes are recovered from the solution by hydrolysis (*Chem. Soc. Trans.*, 1884, 148).

The acid should be placed together with the hydrocarbon in a vessel which can be closed—a stoppered bottle if a moderate quantity is to be treated, or a copper can if the quantity be large. To ensure intimate contact, the vessel is then very vigorously shaken. In the first instance cold acid may be used, as heat is developed by the dissolution of the more easily attacked hydrocarbons; afterwards the mixture of acid and hydrocarbon should be heated to 60—70°. An insufficient quantity of acid is used in the first treatment, and the unattacked hydrocarbon is afterwards shaken with fresh acid; finally it is violently shaken with weakly fuming acid in order to remove all the benzene. Care must be taken in doing this, as the action of the fuming acid usually gives rise to the production of gas—sulphur dioxide.

10. The residual unattacked hydrocarbon is then mixed with a little

alkali and steam-distilled; the product is a brilliant colourless liquid, having the pleasant sweet odour characteristic of a pure paraffin.

11. On hydrolysing the crude mixture of sulphonic acids, after the whole of the benzenoid hydrocarbons have been recovered, a considerable amount of black carbonaceous matter remains with the acid; we have always regarded this as formed from products of the polymerisation of unsaturated hydrocarbons by the dilute acid during the first treatment.

12. The method described is that which renders it possible to separate the whole of the benzenoid hydrocarbons from the original oil-gas products. Much of the benzene, may, however, be obtained without destroying the unsaturated hydrocarbons by refrigerating the appropriate fraction of the liquid deposited on compression of the gas or of the steam distillate from the tar. And it is scarcely necessary to point out, that either separate fractions of the original crude materials, or the crude materials as a whole, may be submitted to treatment in the above manner.

13. To separate the various constituents of the complex mixture of benzenoid hydrocarbons thus obtained, it is fractionally distilled. From the lowest fraction a considerable amount of benzene may easily be frozen out. To separate the toluene, the fractions boiling below 115°, from which no more benzene can be obtained by refrigeration, are shaken with hot concentrated sulphuric acid: as benzene is less readily attacked than toluene, it is possible by fractional treatment with the acid to dissolve chiefly the latter, leaving a residue from which a further quantity of benzene may be crystallised out. The mixture of sulphonic acids with sulphuric acid is poured into water, the solution neutralised with whiting paste, and the resulting calcium salts are then converted into potassium salts, &c.; the liquid when sufficiently concentrated deposits a large crop of the characteristic crystals of potassium tolueneparasulphonate, which are recrystallised and hydrolysed to recover the toluene.

14. The xylenes were separated by Jacobsen's method (*Ber.*, **10**, 1009) from the fractions boiling at 135—145°. *Metaxylene* was identified by conversion into its characteristic trinitro-derivative; independent evidence of its presence was afforded by the production of metatoluic acid in large quantity on oxidation of the fractions collected between 135—145° of the original steam distillate from the oil-gas tar. *Paraxylene* was obtained as sodium paraxylenesulphonate, $C_8H_9{\cdot}SO_3Na{\cdot}H_2O$; and paratoluic acid was obtained on oxidation of the hydrocarbon separated by hydrolysis of this salt. *Orthoxylene* was separated in the form of the highly characteristic sodium orthoxylenesulphonate, $C_8H_9{\cdot}SO_3Na{\cdot}5H_2O$. The three isomeric xylenes appear to us to occur in the oil-gas product very much in the proportions in which

they ordinarily occur in coal-tar xylene, metaxylene being by far the most abundant, and paraxylene the least abundant.

15. Mesitylene and pseudocumene were separated from the fractions boiling between 155—175° by our method of fractional hydrolysis, the hydrocarbon being for this purpose dissolved in sulphuric acid, the solution diluted with water, and steam passed into it at a temperature not exceeding 100—105°. The hydrocarbon thus separated was then reconverted into sulphonic acid; the barium salt of the acid was almost pure mesitylenesulphonate, $(C_9H_{11}\cdot SO_3)_2Ba\cdot H_2O$, which is a very characteristic salt. The equally characteristic potassium salt was also prepared.

After separation of the main bulk of the mesitylene, the temperature was raised, and the whole of the hydrocarbon present separated by hydrolysis; it was then reconverted into sulphonic acid, and the latter several times recrystallised from dilute sulphuric acid, as recommended by Jacobsen (*Annalen*, **184**, 198). In this way a considerable quantity of pure pseudocumenesulphonic acid was readily obtained. The hydrocarbon separated from it had a constant boiling point, and the trinitro- and tribromo-derivative prepared from it had all the properties of these derivatives of pseudocumene.

Mesitylene and pseudocumene are, we think, also present in about the same relative proportions in oil-gas tar as in coal-tar, but it is much easier to separate them from the former on account of the absence of basic compounds.

16. The fractions 180—190° and 190—200° were separately converted into sulphonic acid, from which barium salts were prepared; the salts did not crystallise well, separating from a hot solution in an apparently amorphous state. The dry salt was highly pulverulent, and much like barium 1:2:3:5tetramethylbenzenesulphonate. The salt obtained from the 180—190° fraction was found to contain 23·97, 24·02, 23·81 per cent. of barium. Theory indicates the presence of 24·33 per cent. barium in the sulphonate of a hydrocarbon of the formula $C_{10}H_{14}$. The magnesium salt of the sulphonic acid prepared from the 180—190° fraction crystallised well in flat needles, containing 24·6 per cent. water and 5·21 per cent. of magnesium; a salt of the formula $(C_{10}H_{13}\cdot SO_3)_2Mg\cdot 8H_2O$ should contain 24·24 per cent. water and 5·33 per cent. magnesium. Magnesium pseudocumenesulphonate was prepared for comparison, and was found to be a very similar salt; it contained 26·32 per cent. of water and 5·56 per cent. magnesium. A salt of the formula $2[(C_9H_{11}\cdot SO_3)_2Mg]\cdot 17H_2O$ would contain 26·61 per cent. water and 5·68 per cent. magnesium. A small quantity of hydrocarbon separated from the barium salt prepared from the 180—190° fraction boiled at 178—188°, chiefly at 180—185°. It gave a solid bromo-derivative which, after recrystalli-

sation from alcohol melted at 215°; after repeated recrystallisation the melting point rose to 232·5°. The analysis of an impure portion of this bromide gave 64·59 per cent. bromine, but only 0·09 gram of substance could be used, and probably this contained tribromopseudocumene; the amount corresponding with the formula $C_{10}H_{11}Br_3$ is 64·69 per cent. bromine.

In the barium salt prepared from the 190—200° fraction 23·12 and 23·36 per cent. of barium was found; a salt of the formula $(C_{11}H_{15}\cdot SO_3)_2Ba$ should contain 23·36 per cent. barium.

These facts leave little doubt that at least one benzene higher in the series than trimethylbenzene is contained in the oil-gas product. Probably isodurene is present, but unfortunately the amount at our disposal was insufficient to enable us to prove this.*

17. A large quantity of naphthalene separates from the fractions collected above 200°. After its removal a comparatively small amount of hydrocarbon is left. Benzene being present in such large amount in the oil-gas product, it appeared not unlikely that diphenyl would also occur in them. Notwithstanding persistent efforts to isolate this hydrocarbon, however, we have entirely failed to discover it in the portions boiling between 250—260°. Hitherto, indeed, we have been unable to determine the nature of any of the benzenoid hydrocarbons of higher boiling point than naphthalene; the quantity obtained is very small, and it is impossible to separate a pure substance by distillation.

II. *Hydrocarbons of the* C_nH_{2n-2} *Series.*

18. The separation and identification of the unsaturated hydrocarbons other than those of the benzenoid series is compassed with difficulty. By determining the amounts of bromine required to saturate the various fractions, it was in the first instance ascertained that not only olefines, but less saturated hydrocarbons were present. Moreover, that there were no true acetylenes among these, that is, hydrocarbons of the form $CH\cdot C\cdot C_nH_{2n+1}$, at once appeared from the fact that ammoniacal cuprous and argentic solutions were without appreciable action upon the liquid condensed from the oil-gas. This conclusion was confirmed by the observation made both at the Mansion House Station Works of the Metropolitan District Railway Company and at the Stratford Works of the Great Eastern Company that the gas

* Since this paper was placed in the printer's hands, K. E. Schulze has announced (*Ber.*, **18**, 3032) the discovery of 1:2:4:5tetramethylbenzene (durene) in coal-tar. It may be added that, in a paper read at the last spring meeting of the Iron and Steel Institute, Dr. Armstrong stated that the oil from the Jameson coke oven contained benzenes different from those in ordinary coal-tar.

itself produced but a very small amount of precipitate in an ammoniacal cuprous solution.

19. On warming the crude liquid obtained from the reservoirs in which the gas is stored, distillation at once sets in, much gas being at first given off; this gas is absorbed by bromine. On steam-distilling the resulting bromide, less than two-thirds passed over as a colourless heavy oil; the residue became almost entirely solid on cooling, and from it a pure substance was readily obtained by crystallisation from alcohol.

In like manner by passing the compressed oil-gas into bromine, a liquid bromide was obtained which was for the most part easily volatile, only about 7 per cent. remaining when oil ceased to distil over; the residue partially solidified on cooling, and from it more than half its weight of a solid bromide was obtained identical with that referred to in the previous paragraph.

The bromide in question crystallised from alcohol in small, glistening plates, exhibiting under the microscope a very irregular outline; it fused at 116°, and volatilised with extreme slowness in a current of steam. The percentage of bromine in it, as determined by Volhard's method of combustion with potassium nitrate and sodium carbonate, &c., was found to be 85·99. Hence there could be little doubt that it was a tetrabromide of the formula $C_4H_6Br_4$, the percentage of bromine in which is 85·55. Judging from its properties, the bromide thus obtained is identical with the crotonylene tetrabromide prepared by Caventou from the liquid deposited on compressing coal-gas.

Theoretically, four distinct hydrocarbons of the formula C_4H_6 are possible, viz.:—

1. Ethylacetylene	CH·CEt.
2. Dimethylacetylene	CMe·CMe.
3. Methylallene	$CHMe{\cdot}C{\cdot}CH_2$.
4. Vinylethylene (dimethyleneethane)	$CH_2{\cdot}CH{\cdot}CH{\cdot}CH_2$.

Ethylacetylene is excluded, as our hydrocarbon is not a true acetylene; the hydrocarbon obtained by Caventou from crude butylene bromide gave a tetrabromide which volatilised somewhat readily in the air, and from Almedingen's experiments there is every reason to suppose that this hydrocarbon was dimethylacetylene (*Ber.*, **14**, 2073). By distilling erythrol with formic acid, Heninger obtained a hydrocarbon of the formula C_4H_6 yielding a bromide similar to that prepared by ourselves and apparently identical with that obtained by Caventou by the decomposition of fusel oil at a red heat and from coal-gas: as this hydrocarbon is formed from erythrol it may almost certainly be regarded as dimethyleneethane or vinylethylene. On inspection of the four formulæ it will be obvious that a study of the

oxidation-products is calculated to afford the required proof: vinylethylene should not yield acetic acid, which would, however, be a product of the oxidation of both dimethylacetylene and methylallene; and ethylacetylene forms propionic acid.

20. To obtain the hydrocarbon for oxidation, we have employed a method which we believe will in the future be of great service in the investigation of unsaturated hydrocarbons. The usual practice is to withdraw the bromine from the bromides of these hydrocarbons by means of sodium, but there are numerous objections to this method: in many cases the change takes place only with difficulty and at a high temperature; in others secondary products are formed owing to the high temperature locally developed; and the sodium usually becomes coated with a protecting layer of bromide. It occurred to us that Gladstone and Tribe's zinc-copper couple might be used with advantage, they having already shown that ethylene and propylene bromides are readily deprived of their bromine by its action in presence of alcohol (*Chem. Soc. J.*, 1874, 406). The results have entirely surpassed our expectations; as in all cases hitherto examined we have obtained a practically theoretical yield of hydrocarbon by merely warming the bromide with alcohol and the couple. Moreover, the hydrocarbon thus recovered has always been found to be identical with that used in preparing the bromide—that is, it again yields the same bromide. Unfortunately this method was not made use of until nearly the close of our experiments; had we known of it earlier, we feel sure that we should have been in a position to throw far more light on the nature of the products of the oil-gas manufacture. We may add that it is our intention fully to inquire into the application of this method to the separation of unsaturated hydrocarbons from their compounds with halogens.

21. The oxidation of the hydrocarbon separated from the bromide $C_4H_6Br_4$ by the action of the zinc-copper couple was effected by displacing part of a 2 per cent. solution of potassium permanganate from a bottle full of it by means of the gas from 50 grams of the bromide—the gas having been collected over water in a holder and left for some time in contact with the water to remove alcohol-vapour. The permanganate was vigorously shaken to bring it into contact with the gas, and the oxidation being completed, sulphuric acid was added and the volatile acid removed by steam-distillation. The distillate was neutralised by the addition of about 1·6 gram of sodium carbonate; the neutral liquid having been concentrated, the required amount of silver nitrate was added, and the solution boiled: an amount of silver was precipitated practically equivalent to the silver nitrate used, and no trace of acetate could be detected in the filtrate.

As formic acid is its oxidation-product, there can be no doubt that the hydrocarbon of the formula C_4H_6 from oil-gas is dimethylene-ethane or vinylethylene, $CH_2{\cdot}CH{\cdot}CH{\cdot}CH_2$.

22. On steam-distilling the bromides prepared from the fractions of the original liquid from the oil-gas reservoir collected within a few degrees on either side of 40°, dark-coloured viscid residues were obtained in which crystals gradually formed. It was easy to separate these mechanically, and to purify them by recrystallisation from alcohol. The pure substance crystallised in long, thin, narrow, well-defined prisms, melting at 115°. Analysis gave results agreeing with the formula $C_5H_8Br_4$; thus:—

Subs.	0·1982	AgBr	0·3828	Bromine	per	cent.	82·19
,,	0·2210	,,	0·4284	,,		,,	82·49
,,	0·2441	,,	0·4734	,,		,,	82·53
,,	0·2544	,,	0·4935	,,		,,	82·55
,,	0·2083	,,	0·4021	,,		,,	82·15
,,	0·2278	H_2O	0·0471	Hydrogen		,,	2·30
,,	0·2612	,,	0·0544	,,		,,	2·31
,,	0·2278	CO_2	0·1322	Carbon		,,	15·82
,,	0·2612	,,	0·1526	,,		,,	15·93

		Percentages.	Mean results.
C_5	59·85	15·47	15·87
H_8	8·00	2·07	2·30
Br_4..........	319·04	82·46	82·38
	386·89	100·00	100·55

23. The hydrocarbon was separated from this bromide by warming it with the zinc-copper couple and alcohol; the amount obtained was almost the theoretical. After several days' digestion with calcium chloride in a sealed tube it was distilled; it boiled almost constantly at about 45°, leaving a few drops of a syrupy residue which exploded when heated on platinum, in this respect behaving somewhat like isoprene. It had the peculiar alliaceous odour so characteristic of the crude liquid deposited from oil-gas. It was reconverted into the original tetrabromide on careful treatment with bromine. It was readily oxidised by a 4 per cent. solution of potassium permanganate: more than half of the volatile acid produced was formic acid, the rest being *pure* acetic acid.

Five hydrocarbons of the formula C_5H_8 are at present known: propylacetylene, isopropylacetylene, ethylmethylacetylene, piperylene and isoprene; ours appears to be a sixth. The first three of these are excluded from consideration on account of their behaviour on

oxidation; moreover, our hydrocarbon is not a true acetylene, and cannot, therefore, be either propyl- or isopropyl-acetylene. Piperylene, according to Hofmann (*Ber.*, **14**, 665), forms a tetrabromide crystallising from alcohol in glistening *plates*. Isoprene yields a liquid bromide. Eight modifications in all are possible of a hydrocarbon of the formula C_5H_8; three of these are derived from acetylene; the formulæ of the remaining five are as follows:—

CH_2	CH_3	CH_3	CH_3	$C(CH_3)_2$
CH	CH	CH_2	CH	C
CH_2	CH	CH_2	C	CH_2
CH	CH	C	CH	
CH_2	CH_2	CH_2	CH_3	
Allylethylene.	Isoallylethylene.	Ethylallene.	Symmetrical dimethylallene.	Unsymmetrical dimethylallene.

Piperylene, according to Ladenburg (*Ber.*, **16**, 2059) is allylethylene; and that this is not the composition of our hydrocarbon may be inferred from the fact that it yields acetic acid on oxidation. Ethylallene is also excluded as it would furnish propionic acid on oxidation. But three formulæ remain therefore, and we incline to select that of isoallylethylene on account of the simple relation which this hydrocarbon bears to normal amylene, from which probably our hydrocarbon is immediately derived:—

$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH{\cdot}CH_2 = \text{Propylethylene.}$$
$$CH_3{\cdot}CH{\cdot}CH{\cdot}CH{\cdot}CH_2 = \text{Isoallylethylene.}$$

If our argument be correct, isoprene must be either symmetrical or unsymmetrical *dimethylallene;* taking into consideration all that is known of the terpenes—to which it is so intimately related—the latter is the more probable. We are now engaged in the study of the hydrocarbons of the formula C_5H_8 in the hope of solving this problem, which is one of considerable importance in connection with the question of the constitution of the hydrocarbons of the formula $C_{10}H_{16}$.

24. A faulty determination of bromine, made by Volhard's method, led us, in the first instance, to regard the bromide just described as identical with Schorlemmer's so-called hexoylene tetrabromide, $C_6H_{10}Br_4$, whose description of this compound tallies very closely with that which we have given of our tetrabromide. Schorlemmer prepared his substance from a fraction boiling at about 80° of the more volatile products of the distillation of boghead cannel; to this he added bromine in excess, and after removing the greater part of the admixed benzene by distillation, he heated the bromide with sodium to regenerate the hydrocarbon; this was again brominated.

The product was an oil from which the solid gradually crystallised out. It may be mentioned that Schorlemmer bases the formula $C_6H_{10}Br_4$ on a single determination of bromine in only 0·1970 gram of substance. In the hope, therefore, of obtaining hexoylene we very carefully fractioned out a portion boiling at about 80—82° from our crude material, and this was brominated; on steam-distilling the product much benzene passed over, then an oily bromide heavier than water, a moderately limpid dark-brown oil remaining; no crystals whatever separated from this, and it was therefore submitted to the action of the zinc-copper couple in presence of alcohol. The regenerated hydrocarbon was again brominated and steam-distilled; very little came over. A minute quantity of solid was, however, deposited in the condenser. The experiment was repeated with a considerable quantity of the fractions collected at 70—80°: after adding excess of bromine, the product was steam-distilled until exhausted; traces of a solid were again obtained. On extracting the residue with alcohol comparatively little dissolved and no crystals could be obtained from the alcoholic extract: the final residue was a carbonaceous mass. The solid referred to crystallised from alcohol in small, hard, well-formed, short prisms melting at 185°; the quantity obtained was too small even for an analysis.

25. In all cases, on steam-distilling the crude bromides from the various fractions, decomposition was observed to take place more or less; and the non-volatile residue from all but the lowest fractions was more or less carbonaceous, and alcohol extracted but very little oily matter, leaving a friable residue. The bromides which are thus decomposed are probably derived from hydrocarbons of the C_nH_{2n-2} series—or in part perhaps from less saturated hydrocarbons—such as Schorlemmer has shown to be present in cannel oils. The polymerides obtained by means of sulphuric acid were precisely of the character of those described by Schorlemmer (*Annalen*, 1866, **139**, 244).

III. *Hydrocarbons of the Olefine group.*

26. Indication of the presence of these hydrocarbons is afforded by the behaviour with bromine especially of the lowest fractions of the "hydrocarbon" deposited during compression of oil-gas; these fractions, if free from benzene, are entirely converted into polymerides and soluble bodies on treatment with sulphuric acid: they therefore consist of unsaturated hydrocarbons, but the amount of bromine which they will absorb is far less than would be the case if they contained only hydrocarbons less rich in hydrogen than the olefines.

To isolate the pure olefines from mixtures such as those with which

we have had to deal, no ordinary method will suffice; had we become aware that the zinc-copper couple was applicable to the separation of unsaturated hydrocarbons from their bromides at an early stage instead of almost at the close of this portion of the investigation, it would undoubtedly have been possible to isolate the olefines; but as it was we were obliged to content ourselves with the proof that olefines were present, and with an indirect determination of their nature.

The method followed consisted in oxidising the various fractions by agitation in a stoppered bottle with a cold 4 per cent. solution of potassium permanganate. In selecting this method of treatment we were guided by the knowledge that the normal olefines—those of the type $C_nH_{2n+1}CH{\cdot}CH_2$—are converted by oxidation into acids of the acetic series of the type $C_nH_{2n+1}COOH$, the CH_2 group being eliminated as formic acid; only true acetylenes—*i.e.*, hydrocarbons of the formula $C_nH_{2n+1}C{\cdot}CH$—yield similar products, and, as these were known to be absent from our crude material, the production of the corresponding acid from a fraction of about the boiling point of any particular normal olefine would be conclusive proof of the presence of that olefine. Thus the normal amylene fraction should yield butyric acid, the normal hexylene fraction valeric acid, &c.

The appropriate fractions having been oxidised, sulphuric acid was added, and the volatile acid separated by steam-distillation; the distillate was neutralised with sodium carbonate, concentrated, and then fractionally precipitated with silver nitrate; the silver precipitates were fractionally extracted with water, the solutions well boiled to decompose formate, and the dissolved salts crystallised out and analysed. When a silver salt of constant composition was obtained, it was converted into the calcium salt, as the lower normal primary acids of the acetic series all furnish characteristic calcium salts.

27. The amylene, hexylene, and heptylene fractions treated in this way gave respectively normal butyric, normal valeric, and normal caproic acids.

The higher fractions were similarly treated, but repeated experiments failed to yield any indication whatever of the presence of olefines higher than heptylene: formic and acetic were the only volatile paraffinoid acids produced—these being associated with the oxidation-products of the benzenoid hydrocarbons present in the fractions examined.

A very careful study of all the various fractions obtained has convinced us that besides the three normal primary olefines above mentioned, no other hydrocarbons of the C_nH_{2n} series, or indeed of any other paraffinoid series, can be present, except such as yield acetic and formic acids on oxidation; and we have no reason to suspect that any olefines other than those mentioned are present in the liquid

products from the manufacture of oil-gas: our opinion being that the acetic acid obtained was derived from hydrocarbons less saturated than the olefines.

28. We have already referred to the presence of the hydrocarbon C_4H_6 in the compressed oil-gas (§ 19), and to the manner in which it was separated from the crude mixture of bromides obtained on passing the gas into bromine. On distilling the steam-distillate from this mixture of bromides some hydrogen bromide was evolved, but after a few distillations the constituent yielding this gas was practically all decomposed. By far the largest amount of the bromide separated by fractional distillation had about the boiling point of ethylene bromide, and a considerable quantity of this compound was crystallised out from this portion of the distillate by refrigeration.

29. The next largest fraction had about the boiling point of methylethylene (propylene) bromide, and we have no doubt that it mainly consisted of this compound, as acetic acid was obtained in large quantity by direct oxidation of this fraction with permanganate.

30. Ethylene and propylene having thus been detected in the oil-gas, and normal amylene, hexylene and heptylene in the liquid deposited from it, it was to be expected that normal butylene was also present. A quantity of about 4000 grams of bromides from the gas gave, however, but a relatively small quantity boiling at a higher temperature than propylene bromide, and as it was impossible to separate a pure product by distillation, the various fractions were directly oxidised with permanganate. The quantities used were:—

59	grams	boiling at	148—153°
42	,,	,,	153—158
14	,,	,,	158—164
51	,,	,,	above 164°.

The acid distillate was treated with lead oxide in the manner recommended by Linnemann (*Annalen*, **160**, 222), in order to separate propionic acid, but this acid could not be detected; in fact, only acetic and formic acids were formed.

We have before mentioned that a considerable quantity of bromides was obtained by passing into bromine the gas given off when we began to distil the liquid deposited from oil-gas on compression, and that at least two-thirds of this was volatilised on steam-distillation, the residue consisting mainly of crotonylene tetrabromide; it is possible that the portion of the mixture of bromides volatile with water-vapour contained butylene bromide, but most unfortunately the whole of this material was lost in the fire which occurred in the laboratory of the London Institution during the course of the investigation.

As butylene has a much lower boiling point than crotonylene, we

should certainly expect to find its bromide among those obtained from oil-gas itself, as a considerable quantity of crotonylene tetrabromide is present; our failure to detect it has led us to consider the evidence advanced by Faraday upon which the discovery of butylene among the oil-gas products is attributed to him, and we are of opinion that it is by no means conclusive. His words are as follows:—

"If a portion of the original liquid be warmed by the hand, or otherwise, and the vapour which passes off be passed through a tube at 0° (Fahr.), very little condensed vapour will go on to the mercurial trough, but there will be found after a time a portion of fluid in the tube distinguished by the following properties. Though a liquid at 0°, it upon slight elevation of temperature begins to boil, and before it has attained 32° is all resolved into vapour or gas. . . . . The sp. gr. of the portion I obtained was between 27 and 28, hydrogen being 1. . . . . When cooled to 0° it condensed again, and inclosed in this state in a tube of known capacity and hermetically sealed up, the bulk of a given weight of the substance at common temperatures was ascertained. This compared with water gave the sp. gr. of the liquid as 0·627 at 54°. . . . . Alcohol dissolves it in large quantity. . . . . Sulphuric acid condenses the gas in very large quantity: 1 volume of the acid condensing above 100 volumes of the vapour. . . . . Great heat is produced during the action; no sulphurous acid is formed; the acid is much blackened, has a peculiar odour, and upon dilution generally becomes turbid, but no gas is evolved. A permanent compound of the acid with carbon and hydrogen is produced, and enters as before mentioned into combination with bases. A mixture of 2 volumes of this vapour with 14 volumes of pure oxygen was made, and a portion detonated in a eudiometer-tube; 8·8 volumes of the mixture diminished by the spark to 5·7 volumes, and these by solution of potash to 1·4 volumes, which were oxygen. Hence 7·4 volumes had been consumed, consisting of:—

Vapour of substance	1·1
Oxygen	6·3
Carbonic acid formed....................	4·3
Oxygen in carbonic acid	4·3
Oxygen combining with hydrogen..........	2·0
Diminution by spark	3·1

This is nearly as if 1 volume of the vapour or gas had required 6 volumes of oxygen, had consumed 4 of them in producing 4 of carbonic acid gas, and had occupied the other 2 by 4 of hydrogen to form water. Upon which view 4 volumes or proportionals of hydrogen = 4, are combined with 4 proportionals of carbon = 24, to form

1 volume of the vapour, the specific gravity of which would therefore be 28. Now this is but little removed from the actual specific gravity obtained by the preceding experiments; and knowing that this vapour must contain small portions of other substances in solution, there appears no reason to doubt that, if obtained pure, it would be found thus constituted. . . . . Chlorine and the vapour were therefore mixed in an exhausted retort: rapid combination took place, much heat was evolved, and a liquor produced resembling hydrochloride of carbon, or the substance obtained by the same process from olefiant gas. . . . . Further, it was composed of nearly equal volumes of the vapour and chlorine; it could not, therefore, be the same as the hydrochloride of carbon from olefiant gas, since it contains twice as much carbon and hydrogen."

Taking into account our own observations, especially the fact that we have failed to detect butylene although crotonylene was obtained in considerable quantity, we are inclined to think that Faraday was the discoverer of crotonylene rather than of butylene. It is obvious that he could not have had a pure substance for examination; the ratio of the density of his gas to that of hydrogen was between 27 and 28, and these are numbers which represent the relative density of crotonylene and butylene respectively; the results of his combustion-analysis are almost equally compatible with either formula, C_4H_6 or C_4H_8, always bearing in mind that probably both propylene and amylene were present as impurities; we are not aware that the behaviour of butylene with sulphuric acid has been studied, but it is scarcely probable that it would be so readily absorbed as Faraday describes; there remains but one fact which undoubtedly lends support to the conclusion that it was butylene, viz., that on mixing it with chlorine a chloride was formed, "composed of nearly equal volumes of the vapour and of chlorine." Our proof of the absence of butylene, it should be added, holds good only on the assumption that the butylene present is *ethylethylene*, as the two dimethylethylenes would yield acetic acid on oxidation. As, however, all the olefines which are proved to have been present are represented by the formula $C_nH_{2n+1}\cdot CH\cdot CH_2$, it does not appear probable that the butylene would form an exception, especially as the crotonylene which is so abundantly contained in oil-gas is indubitably a derivative of normal butylene.

IV. *Hydrocarbons insoluble in sulphuric acid.*

31. Our method of separating these hydrocarbons has already been described (§§ 7—10). They are contained almost exclusively in the portion boiling above 150° of the steam-distillate from oil-gas tar: for example, about 1800 c.c. of fractions boiling at 105—130° gave after

exhaustive treatment with sulphuric acid only 6 grams of insoluble hydrocarbons boiling at about 125—140°.

As far as possible, with the limited amount of material at our disposal, the attempt was made to separate the mixture into its constituents by fractional distillation; but no very decided separation was accomplished. Three fractions were analysed with the following results:—

	160—165°.	180—185°.	200—205°.
Carbon percentage	85·33	85·37	85·27
	—	85·26	85·70
	—	85·63	85·50
	—	—	85·39
Hydrogen percentage	14·80	14·74	14·32
,, ,,	—	14·73	—
Relative density, $\frac{0°}{0°}$	0·7775	0·7886	0·8050
,, ,, $\frac{20°}{20°}$	0·7637	0·7768	0·7980

The general mean of the eight carbon determinations is 85·43 per cent., and of the four hydrogen determinations* 14·63 per cent. These numbers are very nearly those which correspond to the formula C_nH_{2n}, viz., 85·56 per cent. carbon and 14·32 per cent. hydrogen. A paraffin of the formula $C_{10}H_{22}$ contains only 84·47 per cent. carbon and 15·53 per cent. hydrogen; while even that of the formula $C_{12}H_{26}$ contains but 84·67 per cent. carbon and 15·33 per cent. hydrogen. The conclusion that our products did not in the main consist of hydrocarbons of the C_nH_{2n+2} type is confirmed by the comparison of our determinations of relative density with the data given by Krafft (*Ber.*, **15**, 1687) for the normal paraffins:—

	B. p.	Density at 0°.	Density at 20°.
$C_{10}H_{22}$	173·0°	0·7452 gram.	0·7304 gram.
$C_{11}H_{24}$	194·5	0·7557 ,,	0·7411 ,,
$C_{12}H_{26}$	214·5	0·7655 ,,	0·7511 ,,

Our figures are in every case considerably higher, and the difference would be greater if a strict comparison were made by calculating the densities corresponding to our relative densities. We are satisfied that this is not due to the presence of benzenoid hydrocarbons, as special care was taken to remove these by treatment with fuming sulphuric and nitric acids followed by distillation from sodium.

* As a warning to those who, like myself, are in the habit of using compressed oxygen for combustions, I may mention that several hydrogen determinations were lost, owing, as was afterwards discovered, to the presence of traces of hydrogen in the oxygen.—H. E. A.

Our figures more nearly agree with those given by Markownikoff and Oglobine (*Ann. Chim. Phys.*, 1884 [6], 2, 372) for the C_nH_{2n} hydrocarbons which they separated—probably in a state of only approximate purity—from Russian petroleum:—

	B. p.	Density at 0°.
$C_{10}H_{20}$..........	161°	0·795 gram.
$C_{11}H_{22}$..........	180	0·8119 ,,
$C_{12}H_{24}$..........	196	0·8025 ,,

Hence we are of opinion that the portion insoluble in sulphuric acid of the steam-distillate from oil-gas tar which we have examined contained both true paraffins and *pseudolefines* such as mainly compose Russian petroleum, the latter being probably the principal constituents.

V. *Summary and discussion of results.*

32. Thus far we have been led to recognise among the products of the manufacture of oil-gas the following hydrocarbons:—

a. Paraffins, of which traces only may be said to be present.

b. "*Pseudolefines*," that is, *saturated* hydrocarbons of the C_nH_{2n} series such as occur in Russian petroleum; these also are present in relatively small amount.

c. Olefines, viz., ethylene, propylene, normal amylene, normal hexylene and normal heptylene, all higher homologues being absent. Ethylene is an important constituent of oil-gas as used, and so also apparently is propylene. The liquid deposited from the crude gas on compression is moderately rich in amylene, hexylene and heptylene.

d. "*Pseudacetylenes*," viz., crotonylene (dimethyleneethane), $CH_2{\cdot}CH{\cdot}CH{\cdot}CH_2$, and isoallylethylene, $CH_3{\cdot}CH{\cdot}CH{\cdot}CH{\cdot}CH_2$. The former is probably an important constituent of the gas, being of high value as an illuminant. Besides these two, both the liquid deposited on compression of the gas and the tar are rich in hydrocarbons identical with, or very closely related to, those discovered by Schorlemmer in cannel oils.

e. Benzenoid hydrocarbons, viz., benzene, toluene, the three isomeric dimethylbenzenes, the two trimethylbenzenes—pseudocumene and mesitylene—and naphthalene; the first mentioned is a specially important constituent in point of quantity. There is reason to believe that other benzenoid hydrocarbons besides these are present, even in the portions of the tar volatile with steam.

33. We have had the opportunity of examining various samples of the oil—shale oil or crude petroleum—used at the works from which we have obtained our materials, and have satisfied ourselves that the

proportion of constituents in them volatile with water-vapour was small, and that they were of a different character from those met with in the bye-products from the manufacture; we have therefore little doubt that practically all the above-mentioned substances are produced in the course of the manufacture of the gas.

34. The paraffins are probably formed in the manner indicated by Thorpe and Young (*Proc. Roy. Soc.*, 1873, **21**, 184), although it is possible that they are in part original constituents of the oil used. It is, however, noteworthy that whereas Thorpe and Young in their investigation of the decomposition of solid paraffins by heat obtained mixtures of lower paraffins and olefines almost in equimolecular proportions from pentane upwards, our material, although rich in amylene and its next two homologues, has not been found to contain the corresponding paraffins.

35. The "pseudolefines" are also more probably products of change than original constituents. But it is to be remembered that according to Beilstein and Kurbatow (*Ber.*, **13**, 2028), American petroleum contains hydrocarbons of the C_nH_{2n} series similar to those in Russian petroleum: hence, assuming our view to be correct, the question arises whether the pseudolefines are formed by simplification of higher pseudolefines or by the removal of hydrogen from corresponding paraffins. Theoretically this question is one of considerable importance, and we are therefore making it the subject of special experimental study.

36. The presence of olefines in products of the distillation of cannel, of coal and of paraffin, has been established by various observers, but no proof of their nature had hitherto been given; it is therefore a matter of interest that those detected by us are all of the type $C_nH_{2n+1}{\cdot}CH{\cdot}CH_2$.

37. Regarding the hydrocarbons of the C_nH_{2n-2} series, it is to be noted that vinylethylene is present in much larger proportion than isoallylethylene, and hence it may be inferred that the former is a much more stable compound. Judging from the behaviour on oxidation of the remaining unsaturated hydrocarbons, which it is to be assumed are to a large extent also members of the C_nH_{2n-2} series, it appears probable that they are formed from corresponding normal paraffins by processes similar to those by which these paraffins are converted into normal olefines and by which vinylethylene and isoallylethylene are formed from the corresponding normal olefines or paraffins.

38. Since Berthelot's discovery of the formation of benzene from acetylene, the benzenoid hydrocarbons have always been regarded as built up from true acetylenes (comp. Jacobsen, *Ber.*, **10**, 853). The fact that true acetylenes are all but absent from oil-gas and the bye-products of its manufacture would lead us to doubt whether this is

so entirely the case; and the question arises whether these hydrocarbons may not also be *directly descended from corresponding paraffins*: whether, for example, benzene may not be obtainable directly from hexane by withdrawal of hydrogen. It is sufficient to point this out, and it would be useless to further discuss the question; but we shall endeavour to solve it by experiment.

It will suffice to have pointed out thus briefly the various problems which await experimental investigation arising out of the examination of the products of the decomposition of petroleum hydrocarbons in the manufacture of oil-gas. By continuing the examination of these products, and also by the study of the changes undergone by a material of more definite composition than the oils used for the purpose, viz., solid paraffin, we hope to obtain facts which will serve to elucidate the nature of many of the changes in hydrocarbons which occur at higher temperatures. The subject is one of very great importance, both as bearing on the discovery of rational methods of coking coal and of manufacturing illuminating gas and also hydrocarbons such as benzene, naphthalene and anthracene. It has undoubtedly also a bearing upon the question as to the origin of the complex mixtures of hydrocarbons such as constitute the different varieties of natural petroleum.

Dr. Armstrong has in his previous paper expressed his thanks to various gentlemen connected with the Great Eastern and Metropolitan District Railways for aid afforded him in carrying out this investigation. We desire on this occasion, however, to thank Mr. W. F. Pettigrew, Engineer in charge of the Great Eastern Company's oil-gas works, for his ever-ready assistance during the past year.

City and Guilds of London Institute,
Central Institution,
December, 1885.

XI.—*The Combustion of Carbonic Oxide and Hydrogen.*

By Harold Dixon, M.A., the Duke of Bedford's Lecturer in Chemistry, Balliol College, Oxford.

Part I.—The Action of Steam on Carbonic Oxide.

In a preliminary account of a research on the incomplete combustion of carbonic oxide and hydrogen, read in 1880 before the British Association, I published the fact that a mixture of carefully dried carbonic oxide and oxygen would not explode when electric sparks were passed through it, but that on the addition of a minute trace of water, or volatile body containing hydrogen, the mixture became inflammable.

To account for this fact, I ventured, after making many experiments, to put forward the hypothesis that, in the ordinary combustion of carbonic oxide, the steam present acts the part of a "carrier of oxygen" by undergoing reductions and successive re-formations :—

$$(1.)\ CO + H_2O = CO_2 + H_2$$
$$(2.)\ 2H_2 + O_2 = 2H_2O.$$

The influence of steam in determining the explosion of carbonic oxide and oxygen has since been confirmed by several experimenters; but, as some* discussion has arisen as to the *mode* in which the steam exerts its influence, I venture to bring before the Society the reasons which appear to me to show that the hypothesis referred to gives the simplest explanation of the observed facts.

Starting on the assumption that dry carbonic oxide and oxygen do not explode, and that the presence of a minute trace of steam confers inflammability on the mixture, I will examine some of the methods by which the steam may be supposed to exert its influence.

The first question to be asked is—Does the steam act in virtue of some property peculiar to itself, or does it share this catalytic power with other gases? To answer this question, the following experiments were made:—Small quantities of different gases were added to separate portions of a non-inflammable mixture of dry carbonic oxide and oxygen, and the spark was then passed. In all cases where a gas containing hydrogen was introduced, the mixture exploded; in all cases where a gas containing no hydrogen was introduced, the mixture did not explode. This argument by the *Joint*

* See Prof. Armstrong's address to Chemical Section of British Association at Aberdeen.

Method becomes stronger the greater the number of instances, positive and negative, adduced, and the nearer the positive and negative instances are in kind to each other. In the following table, under "positive instances" is given the composition of those gases, the presence of which determined the explosion of dry carbonic oxide and oxygen; under "negative instances" is given the composition of those gases which did not determine the explosion:—

Positive instances.	Negative instances.
H_2O	
	.... SO_2.
H_2S	
	.... CS_2.
H_4C_2	
	.... CO_2.
H_2CO_2	
	.... N_2O.
H_3N	
	.... C_2N_2.
$H_{12}C_5$	
	.... CCl_4.
HCl	

Thus whilst an oxide of hydrogen and sulphide of hydrogen both determined the explosion, a third gas composed of sulphur and oxygen did not; whilst a sulphide of hydrogen and a carbide of hydrogen both determined the explosion, a third gas composed of sulphur and carbon did not. Oxygen, sulphur, carbon, nitrogen, and chlorine when combined one with the other, had no action; the same elements combined with hydrogen determined the explosion. Thus only steam—or bodies which form steam under the conditions of the experiment—were found capable of determining the explosion; other gaseous bodies, which differ from the former in not forming steam, were found to have no action. The conclusion is irresistible that the steam does not act as a mere "third body," but, in virtue of its own peculiar chemical properties.

It being shown, then, that steam determines the explosion of carbonic oxide and oxygen in virtue of its chemical properties, the second question is—Does the steam act in some unknown way, by its presence, without undergoing chemical change, or does it undergo a cycle of chemical reactions whereby it gives up oxygen to the carbonic oxide, and returns to its original state? To this question, I believe, no

absolute answer can be given with our present knowledge, for we have no *direct* evidence that the steam is chemically changed during the explosion. But if it can be shown that such a cycle of chemical reactions can take place under the conditions of the experiment, then it is reasonable to prefer an explanation which accounts for the action by known forces, to an explanation which involves the existence of unknown forces. Such a cycle *can* occur, and, as I shall show later on, there is strong experimental evidence against the mere "contact" action of steam.

What then are the reactions by which steam can convey oxygen to carbonic oxide? My hypothesis is that the carbonic oxide is oxidised by the steam in the path of the spark, and that the hydrogen set free unites with oxygen to form steam at a high temperature; the steam so produced acts on more carbonic oxide, and so on, until all the oxygen or carbonic oxide is used up. It is necessary for this complex change that carbonic oxide should decompose steam at the temperature reached in the explosion, and that hydrogen should unite with oxygen under the same conditions. These two reactions are fundamental. If either of them is proved not to occur under the conditions of the experiment, the hypothesis falls to the ground. In a memoir "On the Conditions of Chemical Change in Gases" (*Phil. Trans.*, 1884), I brought forward experiments which appeared to me to establish these two reactions: for (1) when carbonic oxide was exploded with defect of oxygen in a moistened eudiometer, the carbonic acid formed was found to be more than twice the oxygen used, and a corresponding quantity of free hydrogen was found to be present in the residue; and (2) in a dry mixture of hydrogen and oxygen an electric spark caused an explosion under a pressure exactly as low as in a damp mixture. But in a recent paper read before the German Chemical Society, Moritz Traube has rejected my explanation on the ground that carbonic oxide does not decompose steam at a high temperature; and he has put forward the hypothesis that the steam determines the explosion by a joint action with the carbonic oxide on the oxygen, whereby the steam is oxidised to hydrogen peroxide, and the carbonic oxide to carbonic acid:—

$$(1.)\ CO + H_2O + O_2 = CO_2 + H_2O_2,$$

and that the peroxide of hydrogen is then reduced to steam by more carbonic oxide:—

$$(2.)\ CO + H_2O_2 = CO_2 + H_2O.$$

Moritz Traube says:—

"When moist carbonic oxide is submitted to the action of induction sparks for several hours, its volume is not altered, and no trace

of carbonic acid and hydrogen are formed. In opposition to Dixon's supposition, hydrogen has the reverse action on carbonic acid, reducing it at a white heat; for if electric sparks are continuously passed through a mixture of carbonic acid and hydrogen, carbonic oxide and steam are formed with a corresponding diminution of volume."

In these positive statements, Traube asserts not only that carbonic oxide does not decompose steam at the temperature caused by the passage of the induction spark, but he argues that the reaction is impossible because the reverse action occurs under the same conditions. I will first deal with these two statements, and afterwards discuss his own explanation.

1. *The Action of Steam on Carbonic Oxide in contact with Red-hot Platinum.*

The oxidation of carbonic oxide by steam at a high temperature was discovered by Grove. In the paper read before the Royal Society in 1846, " On certain Phenomena of Voltaic Ignition and the Decomposition of Water by Heat," which formed the Bakerian Lecture for 1847, Grove describes two experiments which completely refute Traube's statements. These two experiments seem to have been obscured by the brilliant discovery to which they led—the decomposition of water at a high temperature. I can find no mention of them in any of the chemical manuals I have consulted. Bunsen when he made his experiments on the incomplete combustion of gases, was unaware of the oxidation of carbonic oxide by steam in an explosion. In 1876 the reaction was rediscovered independently by Horstmann and myself in repeating Bunsen's experiments. In the work I have lately been engaged in—viz., heating a coil of platinum wire first in carbonic oxide and steam, and then in carbonic acid and hydrogen, I have been unconsciously repeating the experiments made by Grove 40 years ago. Employing the current from the nitric acid battery he had invented a few years previously, Grove heated a loop of platinum wire sealed into a glass eudiometer containing various gases :—

"Hydrogen and carbonic acid mixed in equal volumes were readily acted on by the ignited wire; they contracted to 0·48 of the original volume; the residue was carbonic oxide; one equivalent of oxygen had therefore united with the hydrogen.

"Carbonic oxide exhibited a remarkable effect, and one which, coupled with the last experiment, gave rise to considerations which mainly led to the results to be detailed in the body of

this paper. Carbonic oxide, very pure, and carefully freed from carbonic acid, was exposed to the ignited wire over distilled water; the gas increased in volume in one experiment to one-third of its original volume—in the greater number of instances to one-fifth: this increase depended upon the intensity of ignition, which it was very difficult to maintain at its maximum on account of the frequent fusions of the platinum wires.

"Here again I had a long research—and many erroneous guesses—which I need not detail. The effect did not take place with perfectly dry gas over mercury, and I thence was led to attribute it to some combination with aqueous vapour; the increase turned out to be occasioned by the formation of carbonic acid. By agitation with caustic potash or lime-water the gas was reduced to exactly its original bulk, but it was now found to be mixed with a volume of hydrogen equal to the volume of carbonic acid by which it had been increased; it was thus perfectly clear that half a volume of oxygen derived from the vapour of the water had combined with one volume of carbonic oxide, and formed one volume of carbonic acid, leaving in place of the carbonic oxide with which it had combined the one volume of hydrogen with which it had been originally associated.

"Comparing the last experiment, viz., that of mixed carbonic acid and hydrogen with this, I was naturally struck with the curious reversal of affinities under circumstances so nearly similar; in the one case hydrogen taking oxygen from carbonic acid to form water, and leaving carbonic oxide; in the other, carbonic oxide taking oxygen from water to form carbonic acid and leaving hydrogen."

This "curious reversal of affinities" led Grove to test the stability of steam at a high temperature—an investigation which is classical in chemistry. The facts themselves are explained by the "Law of Mass." When carbonic oxide and steam are heated they react to form carbonic acid and hydrogen; the carbonic acid and hydrogen so produced react to form carbonic oxide and steam. At a certain point in the decomposition (depending on the conditions of the experiment) the rate of decomposition is equalled by the rate of recomposition; the mixture then remains in equilibrium. So that if a platinum wire is heated in a mixture of carbonic oxide and steam, carbonic acid and hydrogen are produced. As the carbonic oxide and steam are exhausted, the rate of this change becomes slower; but as the carbonic acid and hydrogen increase, the rate of the inverse change becomes quicker. An equilibrium is therefore reached when the two inverse changes take place at equal rates, and it is immaterial which pair of

gases are present to start with; the same equilibrium is reached when carbonic oxide is heated in steam, or carbonic acid is heated in hydrogen.

The carbonic oxide employed in the following experiments was prepared from anhydrous magnesium formate; the carbonic acid was prepared by the action of dilute hydric sulphate on powdered Iceland spar; the oxygen by heating well-dried potassium chlorate: the hydrogen by electrolysis of dilute hydric sulphate. The gases were collected over mercury and dried by anhydrous phosphoric acid.

Into a straight glass eudiometer two coils of platinum were attached to thick platinum pieces, AA′, BB′, sealed into the glass. A current from three Grove cells served to heat both coils to bright redness. A small ring of gas-jets, C, surrounding the eudiometer served to keep hot the top of the mercury column and the glass between the mercury and the coils.

In the first experiment the current was diminished until the coils were just invisible in the dark. The volume of carbonic oxide and steam remained unaltered. When the coils were visible in the dark a very slight expansion was noticed. On heating the coils to dull redness the volume gradually increased and became constant after four hours. On passing up into the tube a few drops of a dilute solution of potash the gases contracted to their original volume.

Expt. 1. Pressure 600 mm.

Platinum Coils heated in Carbonic Oxide and Steam to Dull Redness.

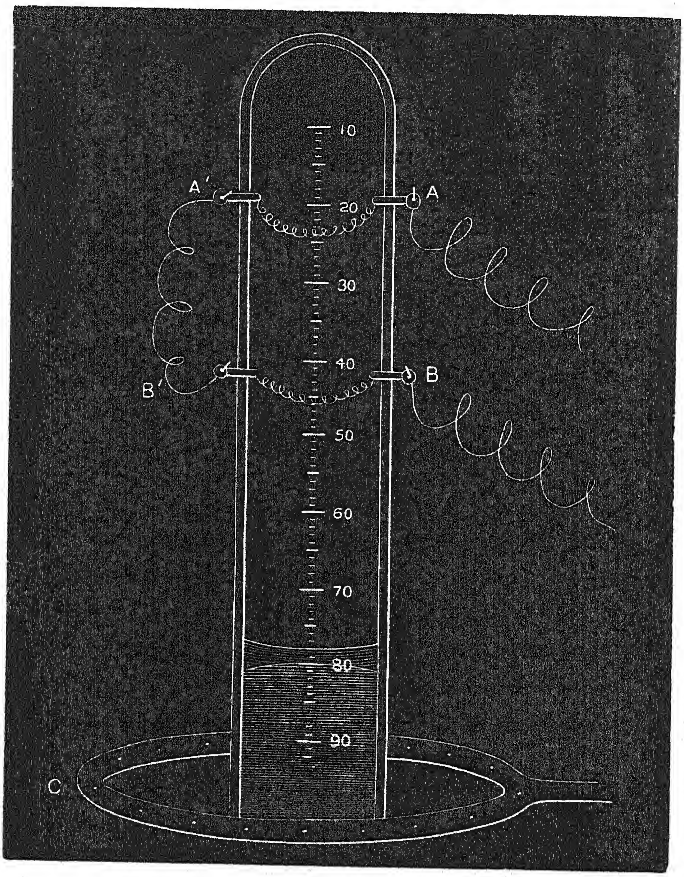
Volume of dry gas reduced to 0° and 760 mm.		Percentage.
Vol. of carbonic oxide at starting ..	22·20 c.c.	100·0
After heating for 1 hour	22·55 "	101·6
" " 2 hours	22·91 "	103·2
" " 4 "	23·35 "	105·2
" " 6 "	23·35 "	105·2
After adding potash..............	22·24 "	100·2

This experiment shows that out of 100 volumes of carbonic oxide, 5·2 volumes were converted into carbonic acid with the liberation of 5·2 volumes of hydrogen.

Expt. 2. Pressure 600 mm.

Platinum Coils heated in Carbonic Oxide and Steam to Redness.

Volume of dry gas reduced to 0° and 760 mm.		Percentage.
Vol. of carbonic oxide at starting ..	23·87 c.c.	100·0
After heating for 1 hour	25·55 "	107·0
" " 4 hours	26·66 "	111·7
" " 6 "	26·64 "	111·6
After adding potash..............	23·87 "	100·0



Eudiometer with Platinum Coils.

Expt. 3. Pressure 600 mm.

Platinum Coils heated in Carbonic Oxide and Steam to Bright Redness.

Volume of dry gas reduced to 0° and 760 mm.		Percentage.
Vol. of carbonic oxide at starting ..	24·94 c.c.	100·0
After heating 4 hours	28·52 ,,	114·3
After adding potash	24·97 ,,	100·1

These experiments show that steam begins to oxidise carbonic oxide at a dull red heat, and that at a bright red heat about one-sixth the carbonic oxide is converted into carbonic acid.

2. *The Action of Hydrogen on Carbonic Acid in contact with Red-hot Platinum.*

In a second series of experiments, equal volumes of dry carbonic acid and hydrogen were brought into the eudiometer, and the two coils were heated in the same way as before.

Platinum Coils heated in Carbonic Acid and Hydrogen to Bright Redness.

Volume of dry gas reduced to 0° C. and 760 mm.		Percentage.
Vol. of carbonic acid..............	15·04 c.c.	100·0
„ hydrogen	15·04 „	100·0
Total	30·08 „	200·0
After heating for 1 hour	19·66 „	130·7
„ „ 4 hours..........	17·15 „	114·0
„ „ 12 „	17·08 „	113·6

On heating the coils, the hydrogen reduces the carbonic acid with the formation of steam and carbonic oxide, the volume of the dry gas therefore diminishes.

In this experiment, in which carbonic acid and hydrogen were taken to start with, the final equilibrium was practically the same as in the previous experiment in which the initial gases were carbonic oxide and steam.

The *limited* reduction of carbonic acid by hydrogen in presence of the products of their reaction serves to confirm, instead of to disprove, the oxidation of carbonic oxide by steam.

In both these experiments, it is possible to push the reaction further by removing one of the products of the change. For instance when steam acts on carbonic oxide and the carbonic acid is removed as it is formed, the whole of the carbonic oxide can be oxidised; and, conversely, when hydrogen acts on carbonic acid and the steam is removed as it is formed, the whole of the carbonic acid can be reduced.

3. *Action of Steam on Carbonic Oxide in presence of Potash.*

Three similar eudiometers, each fitted with a single coil of platinum wire, were charged with an equal volume of carbonic oxide. Some dilute solution of potash was introduced into the three tubes, and the wires were heated. After four hours' heating, the gases in the first tube were analysed; after 16 hours' heating, the gases in the second tube were analysed; and after 64 hours' heating, the gases in the third tube were analysed.

	1. After 4 hours' heating.	2. After 16 hours' heating.	3. After 64 hours' heating.
Carbonic oxide ..	75·2	39·5	29·9
Hydrogen	24·8	60·5	70·1
	100·0	100·0	100·0

In a second experiment, a eudiometer with two coils was used, and the wires were kept hotter than in the previous series. After four hours' heating, one-third of the gases was removed, and the remainder was heated for 12 hours longer. Then half this remainder was removed, and the residue was heated for 16 hours longer.

	1. After 4 hours' heating.	2. After 16 hours' heating.	3. After 32 hours' heating.
Carbonic oxide ..	15·0	2·8	0·8
Hydrogen	85·0	97·2	99·2
	100·0	100·0	100·0

These experiments show that, when the carbonic acid formed is removed from the sphere of action, carbonic oxide may be entirely oxidised by excess of steam.

4. *Action of Hydrogen on Carbonic Acid in presence of Anhydrous Phosphoric Acid.*

Dry carbonic acid was mixed with an excess of dry hydrogen in the eudiometer, and several short sticks of anhydrous phosphoric acid were introduced into the gases. After the volume of the gases had been measured, the coils were heated to redness. From time to time the eudiometer was cooled and the contraction observed. After heating for 40 hours, all but 0·4 per cent. of the carbonic acid had been reduced.

Platinum Coils heated to Redness in Carbonic Acid and Hydrogen in presence of P_2O_5.

Volume of dry gas reduced to 0° and 760 mm.		Percentage.
Vol. of carbonic acid..............	9·49 c.c.	100·0
Vol. of hydrogen	14·67 „	154·6
Total	24·16 „	254·6
After heating for 40 hours	14·71 „	155·0
Contraction	9·45 „	99·6

5. *The Action of Induction Sparks on Carbonic Oxide and Steam.*

The fact that steam oxidises carbonic oxide when induction sparks are passed through the mixed gases was discovered by Buff and Hofmann,* who also confirmed Grove's observation that an incandescent platinum wire transforms carbonic oxide, when confined over water, into carbonic acid. Buff and Hofmann give no numbers. In repeating these experiments, sparks from an induction coil were passed through carbonic oxide and steam between two spheres of platinum-iridium 2 mm. apart. The volume increased rapidly at first, but after an hour remained nearly constant. On adding potash, after 12 hours' sparking, the gases contracted to less than their original volume, showing that some other gas besides carbonic acid had been formed. The solution was tested, and was found to give all the reactions of a formate.

Volume of dry gas reduced to 0° and 760 mm.		Percentage.
Vol. of carbonic oxide at starting ..	18·80 c.c.	100·0
After 1 hour sparking	19·48 ,,	103·6
After 12 hours' sparking	19·60 ,,	104·3
After adding potash	15·78 ,,	83·9

In another experiment, a large Leyden jar was connected with the secondary coil of the Ruhmkorff, and very powerful sparks were passed from this apparatus through the mixture of carbonic oxide and steam. The mixture expanded to about the same extent as before, but the glass near the wires was covered with a thick black deposit, which proved to be nearly all carbon. On heating the deposit in the air it glowed and disappeared, leaving a small grey metallic residue, no doubt volatilised from the wires. When potash solution was added to the mixture, the gases, as before, contracted to less than their original volume; but the solution when tested showed that not more than a trace of formate was present. Some carbonic oxide had, therefore, been decomposed with the formation of carbon and carbonic acid. It appears from this experiment that the decomposition of carbonic oxide, which quickly reaches its limit in the dry gas,† takes place to a much larger extent when the liberated oxygen is removed by union with undecomposed carbonic oxide in presence of steam.

* "On the Decomposition of Gaseous Compounds." Buff and Hofmann (*J. Chem. Soc.*, 12, 282).

† When sparks from a Leyden jar were sent through dry carbonic oxide, a slight decomposition took place amounting to about 0·5 per cent. of the original gas.

Powerful Sparks through Carbonic Oxide and Steam.

Volume reduced to 0° and 760 mm.		Percentage.
Vol. of carbonic oxide at starting ..	22·66 c.c.	100·0
After 16 hours' sparking..........	23·72 „	104·7
After addition of potash	19·45 „	85·8

In another experiment, sparks from the Leyden jar were passed for one hour through carbonic oxide and steam; the volume expanded about 4 per cent., but no trace of formate could be detected in the tube.

6. *The Action of Induction Sparks on Carbonic Acid and Hydrogen.*

When induction sparks were passed through a mixture of carbonic acid and hydrogen, in which the hydrogen was in slight excess, the volume quickly contracted, and after three hours only 6·4 per cent. of the carbonic acid remained undecomposed, as shown by the contraction on adding potash. A trace of formate was found in the solution, so that the carbonic acid remaining was probably less than 6 per cent. The sparking caused a very slight yellow deposit on the glass near the wires.

Volumes reduced to 0° C. and 760 mm.		Percentage.
Vol. of carbonic acid at starting ..	22·86 c.c.	100·0
Vol. of hydrogen at starting	23·37 „	102·2
Total	46·23 „	202·2
Vol. after 1 hour sparking	25·05 „	109·6
„ 3 hours' sparking	24·70 „	108·0
„ adding potash	23·24 „	101·6
Contraction on adding potash......	1·46 „	6·4

7. *The Incomplete Combustion of Carbonic Oxide in presence of varying Quantities of Steam.*

At the beginning of this paper, I mentioned an experiment which showed that when carbonic acid was exploded with insufficient oxygen to completely burn it in a moist eudiometer, the excess of carbonic oxide reacted with the steam at the high temperature produced to form carbonic acid and hydrogen. With the small quantity of steam present at ordinary temperatures, only a small quantity of free hydrogen is so produced; but by raising the temperature of the eudiometer the proportion of steam can be increased at pleasure, and a proportionately large quantity of hydrogen is then found in the residue. A mixture of carbonic oxide and oxygen was made in the

proportion of about 3 to 1. Half of this mixture was fired in a eudiometer saturated with steam at 52° C.; the second half of the mixture was fired under the same pressure, but saturated with steam at a temperature of 68°. The number of steam molecules in the first case was half that of the oxygen; in the second case the number of steam molecules present was the same as that of the oxygen. In the following table the results of these experiments are given, together with those of the original experiment at the ordinary temperature.

Expt. 1.

At 15°. *Tension of Steam* 13 *mm.*

Before the explosion.			After the explosion.		
CO.	O_2.	H_2O.	CO_2.	CO.	H_2.
273·7	100	10?	203	70·7	3·0

Analysis of Residue.

	Found.	Calculated.
CO	70·7	70·7
H_2	2·9	3·0

Expt. 2.

At 52°. *Tension of Steam* 102 *mm.*

Before the explosion.			After the explosion.		
CO.	O_2.	H_2O.	CO_2.	CO.	H_2.
296·8	100	50	211·4	85·4	11·4

Analysis of Residue.

	Found.	Calculated.
CO	85·2	85·4
H_2	11·6	11·4

Expt. 3.

At 68°. Tension of Steam 214 mm.

Before the explosion.			After the explosion.		
CO.	O_2.	H_2O.	CO_2.	CO.	H_2.
296·8	100	100	221·1	75·7	21·1

Analysis of Residue.

	Found.	Calculated.
CO	76·0	75·7
H_2	21·4	21·1

Although some of the water on the sides of the eudiometer was no doubt evaporated during these explosions, and took part in the reaction, the experiments bring out clearly the fact that as the quantity of steam is increased the quantity of carbonic oxide oxidised by it increases also. In the last experiment more than 10 per cent. of the carbonic acid formed was owing to the action of the steam on the carbonic oxide.

It has thus, I think, been amply proved by different experimenters that when steam and carbonic oxide are heated together, either by an induction spark or by a red-hot coil of platinum, or by heated gases in their neighbourhood—the steam oxidises some of the carbonic oxide; and, if fresh proof were required, it has been afforded in a paper (*Ber.*, 1885, 2894) just published by Naumann and Pistor. Since my experiments were made, these chemists have shown that when carbonic oxide and steam are heated in a tube below 580° no reaction takes place; a little above 600° the action begins, and at 950° 10½ per cent. of the carbonic oxide is oxidised to carbonic acid.*

Traube's Hypothesis.

That a trace of peroxide is found on the sides of a moistened jar held over a lighted jet of carbonic oxide is put forward by Traube as

* Under other conditions the equilibrium may be very different. Thus Maquenne (*Compt. rend.*, **96**, 63) found that when carbonic oxide and steam were submitted to the silent electric discharge at a low pressure, 96 to 97 per cent. of the carbonic oxide was turned into carbonic acid.

evidence that the burning of carbonic oxide is brought about by the formation and decomposition of peroxide of hydrogen according to the two equations—

$$(1.)\ CO + H_2O + O_2 = CO_2 + H_2O_2,$$
$$(2.)\ CO + H_2O_2 = CO_2 + H_2O.$$

Now as Traube considers that peroxide is invariably formed when hydrogen burns with oxygen, the fact of peroxide being produced when carbonic oxide burns in the air might equally well have been used by him as an argument that there is hydrogen uniting with oxygen in the flame, and that, therefore, the steam had been decomposed by the carbonic oxide. But as Traube had (wrongly) concluded that carbonic oxide does not decompose steam at a high temperature, such an interpretation was not open to him.

The fact that hydrogen peroxide is found under the conditions of Traube's experiment is no proof that the carbonic oxide is oxidised by peroxide of hydrogen; the evidence advanced for such a reaction is no stronger than could probably be advanced for several other reactions. For instance, formic acid is produced when induction sparks are passed through carbonic oxide and steam; formic acid is oxidised to steam and carbonic acid by oxygen; and *dry* carbonic oxide and oxygen explode in presence of formic acid. These are facts which might be urged with at least equal plausibility to show that carbonic oxide is oxidised by the alternate formation and decomposition of formic acid according to the equations—

$$(1.)\ CO + H_2O = H{\cdot}COOH,$$
$$(2.)\ 2H{\cdot}COOH + O_2 = 2CO_2 + 2H_2O.$$

This interpretation, however, of the function of the steam is not open to us, because it has been shown that formic acid is not produced either by a very powerful spark or by a red-hot platinum wire in carbonic oxide and steam, whereas both the powerful spark and the red-hot wire cause the explosion of moist carbonic oxide and oxygen.

The formation of hydrogen peroxide under the conditions described by Traube seems to be due to the heating of the water by the carbonic oxide flame burning in air, as I shall show in Part II.

Part II.—The Action of Hydrogen on Oxygen.

The hypothesis I have put forward as to the manner in which the presence of steam determines the explosion of carbonic oxide and oxygen has thus been verified to this extent—that some of the steam present would certainly be decomposed in the region of ignition, with the formation of carbonic acid and free hydrogen. It remains to

answer the question, Does this hydrogen unite directly with the oxygen present to form steam? Traube, who finds that peroxide of hydrogen is formed in considerable quantity when the steam from a hydrogen flame is rapidly condensed, by making the lighted jet dip into water, concludes that hydrogen and oxygen do not unite directly to form steam, but that they either react directly to form peroxide of hydrogen, or that hydrogen, oxygen, and steam react together to form water and the peroxide, which is in either case then decomposed by hydrogen:—

$$(1.)\ H_2 + H_2O + O_2 = H_2O + H_2O_2,$$
$$(2.)\ H_2 + H_2O_2 = H_2O + H_2O.$$

It is certainly true that hydrogen peroxide is formed in considerable quantity when a lighted jet of hydrogen dips into pure water. I have confirmed this observation of Traube's several times. But it is also equally true that a lighted jet of pure cyanogen gas playing on the surface of pure water produces a considerable quantity of hydrogen peroxide. Now, I have found that cyanogen, *carefully dried by anhydrous phosphoric acid*, burns in air or oxygen, the presence of steam being unnecessary for its combustion. The formation of hydrogen peroxide appears, therefore, to be due to the heating effect of the cyanogen flame; and the same explanation accounts for its formation by a lighted jet of hydrogen or of carbonic oxide. The following experiment shows that when a portion of pure water is evaporated in air, hydrogen peroxide is found in the residue. 10 c.c. of pure water quite free from peroxide was heated in a porcelain crucible by means of hot sand. No flame or burning body was near the crucible. When 8 c.c. had evaporated the residue gave the reactions of hydrogen peroxide strongly marked. It would seem, then, that the formation of hydrogen peroxide is due to a secondary reaction, and no argument as to the union of oxygen and hydrogen can be drawn from its presence in condensed steam.

I have found that a mixture of hydrogen and oxygen dried by long contact with anhydrous phosphoric acid is exploded by the passage of an electric spark between terminals either of platinum, or of silver, or of aluminium. The platinum terminals had been previously heated in oxygen in presence of phosphoric acid, the silver terminals had been previously heated in hydrogen in presence of phosphoric acid, and the aluminium terminals had been subjected to both processes, for the purpose of preventing the formation of steam at the passage of the spark by hydrogen or oxygen occluded in the metal. A platinum coil, previously heated to whiteness in oxygen in presence of phosphoric acid, when raised to a red heat, after the addition of hydrogen, instantly exploded the mixture. Although

these experiments do not show conclusively that hydrogen unites directly with oxygen at a high temperature without the intervention of steam, I think they make it *probable* that both under the influence of the spark, and in the presence of red-hot platinum, hydrogen and oxygen do unite directly. Once the reaction is begun, no other steam but that being formed in the reaction is necessary to propagate the explosion. There can be no doubt, I think, on this point. For (1) when a mixture of hydrogen and oxygen has its pressure gradually raised until a spark causes an explosion, the pressure at which it inflames is the same whether the mixture be well dried or damp; and (2) the explosion travels as fast in a well-dried mixture as in a damp mixture. Again, the experiments of Berthelot and Vieille (*Compt. rend.*, **95**, 151) have shown that the rate of the "explosive wave" in hydrogen and oxygen is identical with the mean velocity of translation of the *steam* molecules formed in the reaction at the maximum temperature of the explosion. This result I have recently confirmed by a concordant series of measurements (*Brit. Assoc. Reports*, 1885).

These experiments show that when hydrogen and oxygen are exploded in a tube, each successive layer is brought to the ignition point by the impact of steam molecules from the layer just burnt. The rate of the explosive wave corresponds with the velocity of *steam molecules*, and not with the velocity of *hydrogen peroxide molecules*, or with a velocity intermediate between these two. Hydrogen appears, therefore, to unite directly with oxygen to form steam when the temperature of the mixture is raised; at all events the reaction takes place *in the presence of steam.*

The hypothesis of alternate reduction and oxidation by which I have explained the action of the steam on carbonic oxide and oxygen has thus been verified to the further extent, that each part of the process has been separately verified. It has been shown that, *under the conditions of the experiment, carbonic oxide is oxidised by steam with the liberation of hydrogen, and that hydrogen unites with oxygen to re-form steam.*

It yet remains to show that these two reactions give the best explanation of the phenomena exhibited in the incomplete combustion of mixtures of carbonic oxide and hydrogen.

The Incomplete Combustion of Carbonic Oxide and Hydrogen.

The experiments of Horstmann (*Annalen*, **190**, 228; *Ber.*, **10**, 1626; **12**, 64) and myself (*Phil. Trans.*, 1884, Part II) on the incomplete combustion of carbonic oxide and hydrogen have, I think, shown conclusively that the final division of the oxygen between the two combustibles depends on an equilibrium being established between the

two opposite chemical changes—the oxidation of carbonic oxide by steam and the reduction of carbonic acid by hydrogen. In this paper, a similar equilibrium has been shown to be established when mixtures either of carbonic oxide and steam, or carbonic acid and hydrogen, are heated by a platinum wire.

Though the establishment of these reactions removes the chief argument for Traube's hypothesis, it might yet be urged that the union of oxygen with carbonic oxide and hydrogen takes place by means of hydrogen peroxide, and that the reactions determining the above equilibrium in an explosion are *subsequent* to the oxidation of the carbonic oxide and hydrogen by the peroxide. The phenomena observed in the incomplete combustion of carbonic oxide and hydrogen are not in accordance with this view.

When a mixture of carbonic oxide and hydrogen is exploded with insufficient oxygen for complete combustion, at a temperature at which no condensation of steam can take place during the reaction, and at a pressure greater than the critical pressure, the product of the carbonic oxide and steam molecules remaining bears a constant ratio to the product of the carbonic acid and hydrogen molecules remaining, whatever the quantities of carbonic oxide and hydrogen taken to start with, and whatever the quantity of oxygen employed, so long as the oxygen taken is less than half the hydrogen:—

$$\frac{CO \times H_2O}{CO_2 \times H} = 4.$$

When the oxygen employed is more than half the hydrogen, then the ratio between the two products (or the coefficient of affinity) is diminished.

My experiments have shown that when a certain percentage of oxygen is used, the proportion of the hydrogen to the carbonic oxide may be continually reduced without altering the coefficient of affinity, until the hydrogen is reduced to *twice* the oxygen; at that point the coefficient drops, and slowly diminishes as the proportion of hydrogen is further reduced. When a different percentage of oxygen is employed, the same phenomena occur; the coefficient is constant until the hydrogen is reduced to *twice* the oxygen, and then the coefficient drops as before. By varying the percentage of oxygen used the lowering of the coefficient may be made to occur with very different proportions of hydrogen in the mixture; and since in all cases the lowering occurs where the hydrogen and oxygen are present in the proportion of 2 to 1, the one fact is shown to be necessarily connected with the other.

Now, this alteration of the coefficient, when the oxygen is just equal to half the hydrogen, follows as a natural consequence from the

hypothesis that the carbonic oxide is oxidised by the alternate reduction and re-formation of steam; it receives no explanation on the hypothesis that carbonic oxide is oxidised by the alternate formation and reduction of peroxide of hydrogen.

The presence of an inert gas, such as nitrogen, among the combustible gases is found to favour the formation of carbonic acid instead of steam, and therefore to lower the coefficient. If the carbonic oxide receives its oxygen only from the steam formed, it follows that when the oxygen taken is more than half the hydrogen, there will be present during part of the reaction an excess of oxygen chemically indifferent to the three other gases present, viz., carbonic oxide, carbonic acid, and steam, and it will only be capable of reacting as the steam is gradually decomposed by the carbonic oxide. No doubt the molecules of steam, as they are first formed, begin to react on the carbonic oxide, but the formation of steam in an explosion is much faster than the formation of carbonic acid, so that during a period which may be a considerable fraction of the whole time during which the gases are reacting, the excess of oxygen is present as an inert gas, diminishing the intensity of the reaction, like nitrogen, and so favouring the formation of carbonic acid. We should expect then to find a lowering of the coefficient to occur whenever the proportion of oxygen approaches to half the hydrogen.

Now, what should be expected if peroxide of hydrogen were the carrier of oxygen? If we suppose with Traube that the oxygen unites simultaneously with hydrogen and steam, and with carbonic oxide and steam, forming steam, carbonic acid, and peroxide of hydrogen:—

$$(\alpha.)\ H_2 + H_2O + O_2 = H_2O + H_2O_2,$$
$$(\alpha')\ CO + H_2O + O_2 = CO_2 + H_2O_2,$$

and that the peroxide is reduced both by the carbonic oxide and hydrogen in excess:—

$$(\beta.)\ H_2 + H_2O_2 = H_2O + H_2O,$$
$$(\beta')\ CO + H_2O_2 = CO_2 + H_2O,$$

then, even if the formation of steam is considerably faster than that of carbonic acid, there will be no *inert* oxygen present during the reaction, for the oxygen will always be in the presence of carbonic oxide and steam, with which it can combine directly. No lowering of the coefficient ought, therefore, to occur. The same argument tells against the "contact theory" of the action of steam in determining the explosion of carbonic oxide and oxygen. If steam acted by its mere presence without entering into chemical reactions with the carbonic oxide and oxygen, there is no apparent reason for a sudden

change in the coefficient, for steam is present in all cases, and sometimes in larger proportion with the lowered coefficient than when the coefficient is normal.

On the other hand, accepting Traube's alternative view that the oxygen unites directly with hydrogen to form peroxide of hydrogen, then, if this reaction is the first to take place, we might expect to find, in the absence of steam, an excess of oxygen *inert* to the remaining gases, viz., carbonic oxide and hydrogen peroxide, and only gradually entering into combination as *steam* was liberated from the peroxide by the action of the carbonic oxide. But in this case the lowering of the coefficient ought to occur when the volume of oxygen is *equal* to the volume of hydrogen taken, and not when it is *half* the hydrogen.

Post Scriptum.—Professor Armstrong's ingenious suggestion that, in a mixture of carbonic oxide and oxygen, the carbonic oxide is oxidised, and the oxygen is hydrogenised simultaneously by the steam present is not, I think, opposed to any of the observed facts. It would account for the lowering of the "coefficient of affinity," when the oxygen is more than half the hydrogen in the incomplete combustion of a mixture of carbonic oxide and hydrogen, if we suppose that the oxygen molecules are unable to react except when they meet with both carbonic oxide and steam molecules simultaneously. Professor Armstrong's explanation involves the simultaneous occurrence of the two reactions which I consider occur successively.

XII.—*The theory of the interaction of carbon monoxide, water and oxygen gases: a note on Mr. H. B. Dixon's paper on the action of carbonic oxide on steam.*

By Henry E. Armstrong.

Mr. H. B. Dixon, in his paper on conditions of chemical change in gases: hydrogen, carbonic oxide, and oxygen (*Phil. Trans.*, 1884), explains the action of steam in determining the union of carbon monoxide with oxygen in the following words (p. 641):—

"When carbonic oxide and oxygen are exploded in a eudiometer, the heat of the spark causes the carbonic oxide in its immediate neighbourhood to decompose the steam . . . and the hydrogen liberated by this reaction unites with the oxygen to re-form

steam. The steam so formed reacts with more carbonic oxide, and so the alternate changes go on until all the carbonie oxide is oxidised, according to the two equations: (1) $CO + H_2O = CO_2 + H_2$; (2) $2H_2 + O_2 = 2H_2O$."

His account of the changes during explosion in a mixture of carbonic oxide with hydrogen and oxygen is worded thus (p. 660) :—

"The explosion starts with the direct union of oxygen and hydrogen, the change proceeding until all the oxygen is converted into steam; as soon as steam is formed by this union it begins to oxidise the carbonic oxide; the carbonic acid so produced is in turn reduced to carbonic oxide by free hydrogen."

In the foregoing paper he has maintained these views in opposition to Traube, and he has also referred to my interpretation of the nature of the influence of water in inducing oxidation of the carbon monoxide, contending that the lowering of the "coefficient of affinity" which is observed if oxygen be present in an explosive mixture of H_2, O_2 and CO to the extent of more than half the volume of the hydrogen is an argument both against Traube and myself.

In my address to the Chemical Section of the British Association at Aberdeen, speaking of Mr. Dixon's discovery of the influence of water on the explosion of a mixture of CO and O_2, I said: "It appears to me that the water may exercise the same kind of action as it (or rather dilute sulphuric acid) exercises in a Grove's gas battery, and that its hydrogen does not become free in any ordinary sense."

In a Grove's gas battery we have dilute sulphuric acid in contact, on the one hand, with hydrogen, and on the other with oxygen; it may be supposed that before the circuit is closed the system is as represented in (1) and that afterwards it is as represented in (2).

$$(1.)\ \begin{array}{c|c|c} O & H_2SO_4 & H_2 \\ \cline{2-3} \vdots & & \\ O & H_2SO_4 & H_2 \end{array}. \qquad (2.)\ \begin{array}{c|c} OH_2 & SO_4H_2 \\ \hline OH_2 & SO_4H_2 \end{array}.$$

The state before and after explosion of a mixture of CO, O_2 and H_2O may be similarly represented, thus :—

$$\begin{array}{c|c|c} O & H_2O & CO \\ \cline{2-3} \vdots & & \\ O & H_2O & CO \end{array}. \qquad \begin{array}{c|c} OH_2 & OCO \\ \hline OH_2 & OCO \end{array}$$

Both Mr. Dixon and I regard the water as the interagent; but while he considers that its oxygen becomes affixed to the CO, and that its hydrogen in consequence becomes *free*, I regard the oxidation of the carbon monoxide by the oxygen of the water as dependent upon the *simultaneous* oxidation of the hydrogen of the water by the free oxygen. (It is, however, I think, conceivable that the influence

exerted by the water may be of a more purely "mechanical" order, viz., that it does exert a mere contact action, serving to bring together the carbon monoxide and oxygen which are straining at each other.)

I do not see that any decision between our rival hypotheses can be based upon the observation that a change in the ratio of $CO_2 \times H_2$ to $CO \times H_2O$—Mr. Dixon's coefficient of affinity—takes place when the oxygen is more than twice the volume of the hydrogen, as the operations are quantitatively identical in the two cases; especially as the coefficient of affinity only has a constant (maximum) value at pressures above that at which its value is independent of the length of the column of gas exploded, which varies for different mixtures.

One of Mr. Dixon's general conclusions (No. 6, p. 675 of his memoir) is that—

> "The presence of an inert gas, such as nitrogen, by diminishing the intensity of the reaction, favours the formation of carbonic acid in preference to steam. When the hydrogen is less than double the oxygen, the excess of oxygen cannot react with any of the three other gases present—carbonic oxide, carbonic acid, and steam—but has to wait until an equal volume of steam is reduced to hydrogen by the carbonic oxide. The excess of inert oxygen has the same effect as the inert nitrogen in favouring the formation of carbonic acid."

It may well be, however, that although the end-effect of the oxygen is the same as that of the nitrogen, it is produced in another way; and Mr. Dixon's conclusion that oxygen is inert towards carbon monoxide, even in presence of water-gas, is entirely based on his mode of interpreting the character of the change. It appears to me that he overrates the importance of the reaction between carbon monoxide and steam: a series of experiments on the explosion of gaseous mixtures of carbon monoxide, water and oxygen would perhaps afford information of value in regard to this point.

XIII.—*On the Use of Ferrous Sulphate in Agriculture.*

By A. B. Griffiths, F.R.S.E., Lecturer on Chemistry, Technical School, Manchester, &c.

In continuation of my experiments on the use of ferrous sulphate as a manure, I have this year observed its effect on wheat crops with the following results:—

Conditions of Growth of the Crops.

I. Two plots of land (exposed to the same rainfall and sunshine) were chosen, both plots being well-drained land.

II. The soils were of the same chemical and mechanical composition.

III. One of the plots was manured with ½ cwt. of ordinary commercial iron sulphate to the acre.

IV. Each plot of land was of the same size, and the same quantity of seed was applied to each. The quality of the seed was the same, being the produce of my last year's crop.

At the end of the season, the following weights were obtained:—

Wheat Crop.

	Plot of land manured *with* iron sulphate.		Plot of land, normal (*i.e.*, *without* iron sulphate).	
	(1.) Weight when gathered.	(2.) Weight when dry.	(1.) Weight when gathered.	(2.) Weight when dry.
Total weight of crop (grain + straw)...	6425 lbs.	5304 lbs.	6460 lbs.	5316 lbs.

The crop of wheat grown by the aid of iron sulphate yielded 32½ bushels of grain; and the crop grown *without* iron sulphate yielded 30 bushels of grain. From the above results (although there is an increase of 2½ bushels of grain produced by the crop on the iron-manured land), I am rather inclined to the opinion I gave in a former paper (*Chem. Soc. J.*, Trans., 1885, 46--55) that an iron manure is *not* as valuable as a plant-food for cereals as for root and leguminous crops.

On submitting the ashes of the plants from each plot of land to careful analysis, I obtained results which do not differ materially from those of last year.

Table I is an analysis of the ash of the entire wheat plants—

TABLE I.—*The Entire Wheat Plants.*

	Grown *with* iron manure.	Grown *without* iron manure.
Iron oxide, Fe_2O_3	2·60	2·19
Potash, K_2O	12·12	11·67
Soda, Na_2O	2·22	2·59
Lime, CaO	3·53	3·60
Magnesia, MgO	5·51	5·53
Silica, SiO_2	64·90	64·99
Phosphoric oxide, P_2O_5	4·59	4·49
Sulphuric oxide, SO_3	4·02	4·05
Chlorine	0·50	0·89
	99·99	100·00

The ash of the leaves gave the following percentage of ferric oxide :—

TABLE II.—*The Leaves of the Wheat Plants.*

	Grown *with* iron manure.	Grown *without* iron manure.
Iron oxide, Fe_2O_3	3·92	1·54

From the above analysis the percentage of iron oxide in the plants grown with iron sulphate was about half a per cent. over those grown on the normal plot of land. The percentage of ferric oxide in the leaves of the crops is larger in those grown on the iron-manure land by $2\frac{1}{4}$ per cent.

Besides my own experiments on cereal crops, Mr. George W. Edgson, of Etton, near Peterborough (an agriculturist of great experience), has applied iron sulphate to several acres of wheat-crops this year (1885). He tells me that this wheat-crop was better than any he has had for very many years, and he "*never saw such clean straw*" in his life, being perfectly free from wheat mildew.

I had the pleasure of seeing these crops last summer, and may remark that they looked the healthiest and finest in the neighbourhood. I have made analyses of the ashes from Mr. Edgson's wheat-crops grown with iron sulphate. The following is the percentage of ferric and phosphoric oxides contained in the ashes :—

TABLE III.—*The Entire Plant* (Mr. Edgson's Crop).

Iron oxide, Fe_2O_3	3·45
Phosphoric oxide, P_2O_5	5·88

TABLE IV.—*The Ash of the Leaves.*

Iron oxide, Fe_2O_3	3·99
Phosphoric oxide, P_2O_5..........	4·97

From the above analyses, it is evident that there is a greater *increase* of ferric oxide than is normally found in the ashes of wheat-crops, and the phosphoric oxide is also increased. It appears that in this case the iron manure has been beneficial—increasing the growth and yield of the wheat-crop. Yet, as far as my own experiments with cereal crops go, I have seen no remarkable increase due to an iron manure. These facts evidently show that some soils are deficient in iron, or, to use the words of M. Ville,* "it may be that more efficacious compounds of iron and manganese exist than those which the soil contains naturally, and whose presence in manures would be followed by an increased yield."

Grass Land.

Mr. Edgson has also used iron sulphate to grass land. A large plot of grass land of his was "infested" with the ordinary moss, and was extremely poor in quality and quantity. After having applied a top-dressing of iron sulphate to this land, the grass turned black after the first rainfall, but in a fortnight became a bright-green colour, and perfectly healthy, and the moss was destroyed. The grass grew well throughout the summer. The bright-green appearance never altered in the least, although the summer was rather a dry one, and other plots of grass land which had received occasional dressings of nitrate of soda were "parched up," more or less, for want of rain.

I have submitted the ashes of the grasses and mosses to analysis, with the following results :—

* "On Artificial Manures," Mr. Crookes' Translation, 2nd Edition, p. 39.

TABLE V.—*Ash of Mosses.*

	Ash of plants *before* addition of $FeSO_4$ to the land.	Ash of plants *after* addition of $FeSO_4$ to the land.
Iron oxide, Fe_2O_3	6·62	11·56
Alumina, Al_2O_3	10·79	10·25
Potash, K_2O	2·48	3·24
Soda, Na_2O	3·40	2·10
Lime, CaO	11·28	10·89
Magnesia, MgO	3·23	3·62
Silica, SiO_2	45·10	41·59
Phosphoric oxide, P_2O_5	3·73	4·03
Sulphuric oxide, SO_3	12·74	11·97
Chlorine	0·61	0·74
	99·98	99·99

TABLE VI.—*Ash of Grasses.*

	Grass from land *not* manured with iron sulphate.	Grass from land manured *with* iron sulphate.
Iron oxide, Fe_2O_3	0·45	2·46
Potash, K_2O	24·92	23·12
Soda, Na_2O	6·21	6·10
Lime, CaO	15·00	14·26
Magnesia, MgO	5·46	4·98
Silica, SiO_2	29·06	29·61
Phosphoric oxide, P_2O_5	5·52	7·21
Sulphuric oxide, SO_3	8·46	7·43
Chlorine	4·92	4·82
	100·00	99·99

It will be seen from the above analyses (Table VI) that grass manured with iron sulphate gives larger amounts of ferric and phosphoric oxides in the ash than the grass before the addition of iron sulphate—hence the healthy appearance (during a rather dry summer) may be due to this circumstance; an iron manure being beneficial for the growth of grass. The analysis of the ashes of the *moss-plants*, after the addition of iron sulphate, shows that the percentage of ferric oxide is 11·56. In a former paper (*Chem. News*, **50**, 193, "Physiological Experiments with Iron Sulphate on Plants"), I found that all the plants I had examined died when they had absorbed iron salts to the extent of yielding 10 *per cent.* of ferric oxide after incineration. Hence the reason the mosses were destroyed (by the iron

sulphate), being plants naturally requiring a large amount of moisture.

Antiseptic Properties of Iron Sulphate and its Action on Vegetable Parasites.

I have already published a paper on the antiseptic properties of iron sulphate (*Chem. News*, **49**, 279; also *Chem. Soc. J.*, Abstr., 1884, 1070) in connection with micro-organisms and the *Peronospora infestans* (potato disease). An aqueous solution containing as little as 0·1 gram of iron sulphate in 100 grams of water has the power of destroying the *Peronospora infestans.* After a careful microscopical study, I have found that iron sulphate attacks the cellulose walls of the hyphæ of peronospora, perforating them. That is, it may act chemically upon the cellulose—or the form of cellulose making up the external walls of this lowly organism.

I have also made a careful microscopical study of the action of iron sulphate on "*wheat-mildew*" in both stages of its life-history. First with the red spores ("rust") of the barberry fungus, which produce hyphæ in the cells of the stem or leaf of a wheat-plant or similar cereals; and also with the two-celled spores of the wheat-mildew which germinate on the leaf of the barberry.

On placing the spores of "rust" and also the two-celled spores of wheat-mildew on slides under the microscope, mounted in a drop of water, then running in between the cover-slips the above solution of iron sulphate, the spores are completely destroyed. Not only the spores, but the hyphæ which they give rise to, are also destroyed by the same solution. Hence from this experiment it will be seen that iron sulphate is a useful agent, besides being a direct plant-food, for it has a remarkable action on parasitic life.

Turning to the more practical side of this investigation, I should recommend the use of a weak solution of iron sulphate to water ordinary farmyard manure before it is applied to the land; for farmyard manure may contain spores from the wheat-straw forming the litter in the farmyard. These and other spores hibernate until the spring (farmyard manure being a medium that rather favours this dormant state than otherwise), and are then ready to live their life-history again.

Potato Crops.

This year I have grown potato crops with iron sulphate along *with* other artificial manures, so as to make a comparison between potato crops growing with the ordinary artificial manures used for potatoes *with* and *without* the addition of iron sulphate. Three plots of well-drained land were chosen, and the soil was of good quality. All were exposed to the same climatic influences (*i.e.*, rainfall and sunshine).

The first plot of land (A) was left normal—not treated with any manure. The second plot of land (B) was manured with—

$$\begin{cases} \text{1 cwt. kainite,} \\ \text{1 cwt. nitrate soda,} \\ \tfrac{1}{2}\text{ cwt. iron sulphate,} \\ \text{2 cwt. superphosphate of lime,} \end{cases}$$

per acre. The third plot (C) was manured with the above constituents (per acre) *minus* the $\frac{1}{2}$ cwt. of iron sulphate.

At the end of the season the following were the results obtained (7 cwt. of tubers were sown on each plot of land) :—

TABLE VII.—*Potato Crops.*

	A.	B.	C.
Tubers	6720 lbs.	19040 lbs.	14023 lbs.
Haulm	2125 „	6231 „	4917 „
Total weight of crop.	8845 lbs.	25271 lbs.	18940 lbs.

From the above, the crop grown with the addition of iron sulphate to the ordinary artificial manure, yielded $8\frac{1}{2}$ tons of potatoes (tubers). The crop grown with the artificial manure *without* iron sulphate yielded only $6\frac{1}{2}$ tons of tubers, while the normal plot of land only gave 3 tons. Hence an iron manure is beneficial for the growth of potato crops—largely increasing the yield and also, I may say in passing, the quality.

I have submitted the ashes of the potato crops to analysis, with the following results :—

TABLE VIII.—*Ash of Potato Tubers.*

	A. Normal plot.	B. Grown on plot manured with $FeSO_4$ and artificial manure.	C. Grown on plot with *only* artificial manure.
Iron oxide, Fe_2O_3	5·15	7·00	5·42
Potash, K_2O...........	53·80	52·91	53·69
Soda, Na_2O	0·71	1·09	1·20
Lime, CaO	3·02	3·14	3·19
Magnesia, MgO	7·94	7·25	7·23
Silica, SiO_2	5·00	5·21	5·21
Phosphoric oxide, P_2O_5 ..	15·63	17·94	16·24
Sulphuric oxide, SO_3	5·21	3·34	4·00
Chlorine	3·50	2·12	3·81
	99·96	100·00	99·99

TABLE IX.—*Ash of Potato (Haulm).*

	A. Normal plot.	B. Grown on plot manured with $FeSO_4$ and artificial manure.	C. Grown on plot with *only* artificial manure.
Iron oxide, Fe_2O_3	1·10	4·23	1·56
Potash, K_2O	28·99	27·86	29·02
Soda, Na_2O	15·52	12·10	14·34
Lime, CaO	17·07	14·92	16·42
Magnesia, MgO	7·90	7·63	7·84
Silica, SiO_2	3·64	4·81	3·59
Phosphoric oxide, P_2O_5...	7·84	9·92	8·32
Sulphuric oxide, SO_3.....	5·64	5·90	5·97
Chlorine	12·30	12·62	12·92
	100·00	99·99	99·98

It will be seen from the analyses of the ashes of the plants that the ferric oxide is increased in the ashes of the crops grown with an iron manure, and also the phosphoric oxide increases as the iron increases. The potato crop grown with the artificial manure, plus ½ cwt. of iron sulphate, gave a much larger yield of produce than either of the other two crops.

Retentive Properties of Iron Sulphate for Ammonia and Phosphoric Acid.

From my previous papers on this subject, and also the present one, it will be observed that all those crops grown with iron sulphate gave an increase of phosphoric acid, P_2O_5, in their ashes over those not so manured. Therefore I am inclined to think, from these practical results, that iron sulphate (or the iron manure) has a retentive property for phosphoric acid contained in soils. Ferrous sulphate has also a retentive property for ammonia contained in soils. This I have proved experimentally, for by preparing a thick layer of soil (placed in a wide glass tube about one yard long) containing iron sulphate, and then allowing a solution of ammonium sulphate to percolate through this layer, a large amount was absorbed—the liquid which came through the soil containing much less ammonium sulphate than the amount in the original solution. Again, when the same quantity of soil (*minus* the iron sulphate) was treated exactly in the same way, a much larger amount of ammonium sulphate was found in the percolated liquor.

Duration of Iron Sulphate in the Soil.

It was at the suggestion of Mr. Bischof, F.I.C., that I should ascertain how long after manuring a soil with ferrous sulphate any ferrous sulphate can be detected in the soil. I have found that after manuring a soil with ferrous sulphate it could be distinctly detected in the soil after the lapse of six weeks.

Method of Applying Iron Sulphate to the Land.

The question "Which is the best way to apply iron sulphate to the land?" has been repeatedly asked by numerous inquirers.

I. I have found it *best* to apply the iron sulphate as a top-dressing to the land after the crops have appeared above the ground. The sulphate is capable of withstanding (during a comparatively *dry* season) beyond a mere superficial oxidation, for some weeks on the surface of the soil—it being gradually dissolved and passing into the soil.

II. The amount of iron sulphate I have used in all my experiments is $\frac{1}{2}$ *cwt. to the acre.*

Sir John B. Lawes, F.R.S., kindly writes me, that he has found that $1\frac{1}{2}$ cwt. of iron sulphate per acre "was rather too much, although it did not kill the plants."

Experiments with Iron Sulphate on Rose-trees.

Last spring I treated several young rose-trees (climbing, about 2 feet in height from the soil) with iron sulphate. By the end of July they had aattined the height of 16 to 20 feet—increasing almost in the same proportion laterally. The rose-trees produced numerous roses of the most perfect form and colour. All new buds produced by these trees resisted the attack of the "green fly." In former years young rose-trees on the same land grew very slowly—some never flowering at all. From these experiments, and also others performed by several friends, I am able to say that iron sulphate is a good manure for rose-trees.

XIV.—*On Multiple Sulphates.*

By EMILY ASTON and SPENCER UMFREVILLE PICKERING, M.A. Oxon., Professor of Chemistry at Bedford College.

THE double sulphates of the type $M''SO_4,M'_2SO_4,6H_2O$, in which M'' represents any metal belonging to the magnesium or copper class, are stated to be able to combine with each other, molecule with molecule, forming multiple sulphates such as

$$(CuSO_4,K_2SO_4,6H_2O,MgSO_4,K_2SO_4,6H_2O),$$
$$(CuSO_4,K_2SO_4,6H_2O,MgSO_4,K_2SO_4,6H_2O,FeSO_4,K_2SO_4,6H_2O),$$

&c., for a description of which we are indebted to Vohl (*Annalen*, **94**, 57), as many as 42 of these "double double" sulphates having been described by him (half of them containing potassium sulphate, and half ammonium sulphate), as well as two "triple double" sulphates, and one "quadruple double" sulphate. They may be regarded as being derived from the double magnesian sulphates such as $CuMg(SO_4)_2,14H_2O$, by the substitution of 2 mols. of potassium or ammonium sulphate for 2 mols. of water, just as the double salts such as $MgSO_4,K_2SO_4,6H_2O$ may be regarded as derived from the single sulphate $MgSO_4,7H_2O$ by the replacement of one of the water molecules in it. Of the double magnesian sulphates, Vohl described two preparations, as well as some double and triple alums.

Being desirous of investigating these complex double salts, with a view to their bearing on the constitution of molecular compounds in general, we attempted to prepare some of them by the simple method employed by Vohl, namely, mixing solutions of the constituent sulphates in the requisite proportions, and leaving the mixture to evaporate spontaneously. The composition of the salt thus formed, however, by no means corresponded to the theoretical numbers, and we were consequently led to undertake an investigation of these substances; this has led to the unexpected conclusion that none of them can well be regarded as definite chemical substances. It is certainly with some diffidence that we venture to throw doubt on the surprisingly accurate analyses of 50 different salts published by Vohl, and we are even unable to explain his results by the fact that he invariably mixed the constituent sulphates in the theoretical proportions, and did not vary the conditions of his experiments, for the very methods employed by him have failed to yield us definite compounds. We can only publish our own results without venturing any explanation of his.*

* With reference to the double salts, see also Hannay, *Chem. Soc. J.*, 1879, Trans., 456; Pickering, *Chem. News*, **52**, 251.

The "double double" salts were the first objects of our inquiries, and three methods of preparing them were adopted, varying in each case the proportions in which the constituents were mixed.

The first of these methods consisted in mixing cold saturated solutions of the constituent sulphates, and examining the crystals which separated on standing, without allowing any evaporation or change of temperature to occur. The second method was that of cooling hot saturated solutions; and the third, allowing the solutions to evaporate spontaneously.

The first salt chosen was the potassium copper magnesium sulphate, of which the theoretical formula is

$$(CuSO_4,K_2SO_4,6H_2O,MgSO_4,K_2SO_4,6H_2O).$$

The method employed in ascertaining the composition of the salt consisted in determining the amount of copper which it contained, this being the only method which could be employed satisfactorily, since the determination of magnesium is most uncertain, and a wide range in the composition of the salt would affect the sulphur or water percentage to a small extent only.

The results of two series of experiments are given in Table I: the wide difference between them is due to the fact that they were not performed at the same temperature, but in themselves they are concordant, and show conclusively that the composition of the crystals varies continuously with the proportion of the constituents taken, and that in no case did any of them agree with the theoretical compound, which should contain 9·375 per cent. of copper oxide; the nearest approach to this was obtained in Experiment 5, where the magnesium taken was over two and a half times as much as the copper. In this and every other case, the potassium sulphate added was sufficient to combine with the whole of the other sulphates present: the actual amount of potassium sulphate taken being 23·7 grams. The colour of the crystals, as well as the amount obtained, varied with the proportions taken.

Table II contains the analyses of salts obtained by cooling hot saturated solutions: in one case only did the crystals correspond in composition to a definite compound, but the other experiments show that this was fortuitous, and that a variation in the proportion of the salts taken produces a variation in the product, just as in the case of cold solutions. A comparison of the results given in this table with those in the previous one shows that temperature has a considerable effect on the nature of the product.

The figures in Table III show that the products obtained by spontaneous evaporation are not more definite than those obtained by the other methods.

TABLE I.—*Potassium, Copper, and Magnesium Sulphate Solutions mixed.*

Solution taken contained Cu : Mg.	Crystals obtained		
	Weighed.	Contained	
		Percentage CuO.	Cu : Mg.
1 ..... 2 : 1	15·0 grams	16·518	10·6 : 1
2 ..... 1 : 1	10·6 "	14·863	4·5 : 1
3 ..... 1 : 2	2·9 "	13·050	2·5 : 1
4 ..... 1 : 1	—	11·205	1·6 : 1
5 ..... 1 : 2·6	—	9·614	1·05 : 1
6 ..... 1 : 5·2	—	5·891	1 : 2·3

TABLE II.—*Hot Solutions of Potassium, Copper, and Magnesium Sulphate cooled.*

Solution taken contained Cu : Mg.	Crystals contained	
	Percentage CuO.	Cu : Mg.
7 ...... 2 : 1	14·709	4·2 : 1
8 ...... 1 : 1	12·478	2·1 : 1
9 ...... 1 : 2	9·433	1 : 1

TABLE III.—*Potassium, Copper, and Magnesium Sulphate Solutions evaporated over Sulphuric Acid.*

Solution taken contained Cu : Mg.	Crystals contained	
	Percentage CuO.	Cu : Mg.
10 ...... 1 : 1	13·958	3·3 : 1
11 ...... 1 : 2	10·965	1·65 : 1

The next salt which was investigated was the supposed copper cobalt compound $CuSO_4,CoSO_4 2K_4SO_4,12H_2O$.

The results obtained on mixing cold saturated solutions of the constituent sulphates as given in Table IV coincide perfectly with those

yielded by the copper magnesium sulphate; the quantity of the crystals, their colour, and their composition varying regularly with the proportions taken, and showing not the slightest indication of the existence of a definite chemical compound. The variation in colour was so distinct, ranging from a dirty blue in Experiment 12 to a strong red in Experiment 19, that analyses were almost superfluous, and only four out of the eight products were analysed.

TABLE IV.—*Potassium, Copper, and Cobalt Sulphate Solutions mixed.*

Solution taken contained Cu : Co.	Crystals obtained		
	Weighed.	Contained.	
		Percentage CuO.	Cu : Co.
12 ... 5 : 1	7·6 grams	14·016	3·55 : 1
13 ... 3 : 1	7·0 "	—	—
14 ... 2 : 1	6·8 "	—	—
15 ... 1·5 : 1	6·6 "	—	—
16 ... 1 : 1	5·9 "	9·571	1·2 : 1
17 ... 1 : 2	5·5 "	6·65	1 : 1·7
18 ... 1 : 3	5·3 "	—	—
19 ... 1 : 5	4·9 "	3·698	1 : 3·86

The results obtained by cooling hot saturated solutions are given in Table V, and those obtained by spontaneous evaporation in Table VI. A regular variation in the colour and composition of the crystals is as well defined here as in the other cases. The solutions mentioned in

TABLE V.—*Hot Solutions of Potassium, Copper, and Cobalt Sulphates cooled.*

Solution taken contained Cu : Co.	Crystals contained	
	Percentage CuO.	Cu : Co.
20 ... 1 : 1	9·874	1·3 : 1
21 ... 1 : 1	Same in colour as No. 20.	—
22 ... 1·5 : 1	Intermediate in colour between Nos. 20 and 23.	—
23 ... 1 : 2	6·169	1 : 1·86
24 ... 1 : 2	Similar in colour to No. 23.	—
25 ... 1 : 2*	As red as No. 19.	—

* With deficit of potassium sulphate.

Table IV were also allowed to evaporate spontaneously, and the crystals thus obtained in every case resembled so nearly the first crops as to be indistinguishable from them.

TABLE VI.—*Potassium, Copper, and Cobalt Sulphate Solutions evaporated spontaneously.*

Solutions taken contained Cu : Co.		Crystals contained	
		Percentage CuO.	Cu : Co.
26	1 : 1	9·78	1·3 : 1
27	1 : 2	6·918	1 : 1·6
28	5 : 1	All exactly the same in colour as those obtained on mixing the saturated solutions in these proportions. See Table IV.	
29	1 : 1		
30	1 : 2		
31	1 : 5		

Table VII contains the analyses of some crystals obtained on evaporating solutions of potassium, cobalt, and magnesium sulphate; these also do not correspond to any precise formula, and become poorer in cobalt as the solution yielding them contains less of that sulphate.

TABLE VII.—*Potassium, Cobalt, and Magnesium Sulphate Solutions evaporated spontaneously.*

Solution taken contained Co : Mg.		Crystals contained Co : Mg.*
32	1 : 1 first crop	1 : 1·37
33	„ second crop	1 : 1·69

* Determined by estimating the water and the sum of the magnesium and potassium sulphates present.

Such being the results obtained with the "double double" sulphates of the supposed type [$M''SO_4,K_2SO_4,6H_2O,M_1''SO_4,K_2SO_4,6H_2O$], it remained to be ascertained whether the salts from which they were said to be derived, [$M''SO_4,7H_2O,M_1''SO_2,7H_2O$], were equally hypothetical.

When saturated solutions of copper and magnesium sulphates are mixed, no crystallisation takes place, consequently the mixtures of these solutions had to be further evaporated. Table VIII contains the results of evaporating them while hot, and allowing them to cool.

Nos. 34 and 35 crystallised in the same form as copper sulphate, and a determination of the water present showed that both the sulphates constituting them contained $5H_2O$, whereas in Nos. 36 and 37 they took the form of magnesium sulphate crystals, each containing $7H_2O$.

TABLE VIII.—*Hot Solutions of Copper and Magnesium Sulphates cooled.*

Solution taken contained Cu : Mg.	Crystals contained	
	Percentage CuO.	Cu : Mg.
34 ..... 2 : 1	31·438	96 : 1
35 ..... 1 : 1	28·71	9·4 : 1
36 ..... 1 : 2	11·716	1 : 1·6
37 ..... 1 : 3	9·612	1 : 2·2

These sulphates show as little tendency to combine in definite proportions as those containing potassium, the composition of the product varying continuously with the proportion in which they are taken: indeed, there even appears to be a marked disinclination to crystallise in equal molecular proportions: it was noticed that the solution containing 1 mol. of each of the metals required much more evaporation than any of the others before crystallisation could be induced, as if, while the opposing forces were equal, the sulphates were uncertain whether to assume the form of the copper or of the magnesium salt, and finally, when they did crystallise, the proportion in which they did so was far from 1 : 1 mol. A similar tendency to avoid a definite composition is observable also in the results obtained by the spontaneous evaporation of these salt solutions as embodied in Table IX. The water determinations are here given, but, owing to the fact that a considerable alteration in the composition of the salt would cause but a small alteration in the percentage of water present, this does not give such a trustworthy method of calculating the composition as the copper percentage does.

Experiments 47 and 48 were performed on very large quantities of the salts, and at a different temperature from that employed in the other experiments.

The results of this examination would prove that salts corresponding to either of the formulæ

$$[(M''SO_4,K_2SO_4,6H_2O)(M_1''SO_4,K_2SO_4,6H_2O)]$$

or $[(M''SO_4,7H_2O)(M_1''SO_4,7H_2O)]$ do not exist, and that similar

TABLE IX.—*Copper and Magnesium Sulphate Solutions evaporated spontaneously.*

Solution taken contained Cu : Mg.	Crystals contained			
	Percentage CuO.	Cu : Mg.	Percentage H_2O.	Cu : Mg.
38 .. 2 : 1	—	—	36·183	100 : 1
39 .. ,, 2nd crop	30·87	33·5 : 1	—	—
40 .. 1 : 1	—	—	36·328	24·3 : 1
41 .. ,, 2nd crop	11·655	1 : 1·6	47·438	—
42 .. ,, 3rd crop	10·890	1 : 1·7	47·416	—
43 .. 1 : 2	11·726	1 : 1·6	47·755	—
44 .. ,, 2nd crop	10·813	1 : 1·8	48·077	—
45 .. 1 : 3	9·693, 9·605 } 9·649	1 : 2·2	48·332	—
46 .. ,, 2nd crop	8·323	1 : 2·7	48·773	—
47 .. 1 : 2	12·745	1 : 1·37	48·171	—
48 .. ,, 2nd crop	12·416	1 : 1·26	—	—

salt molecules, such as are here supposed to be united, have no tendency to combine with each other, were it not for two facts, which tend to show the contrary. When saturated solutions of potassium and copper sulphates are mixed, a certain amount of the double salt separates; in the case of potassium and magnesium sulphates this is not so (this vol., p. 16); but on mixing all three of these sulphates the copper salt carries down with it a considerable quantity of the magnesium salt. The second fact is that, with the copper and magnesium sulphates, either, when in excess, will induce the other to crystallise out in a form, and with a proportion of water foreign to its nature.

These are the only two pleas which we can put forward for regarding either of these salts as chemical compounds; and, even if they be accepted, we can certainly not call them *definite* compounds, but substances more nearly resembling the product of the crystallisation of two isomorphous salts.

Note.—Since writing the above, my attention has been called to an investigation of the potassium cobalt nickel sulphates by J. M. Thomson (*Brit. Assoc. Rep.*, 1877, 209), the results of which are entirely in accordance with the experiments here given. Thomson found that the successive crops of crystals deposited on evaporating a saturated solution of the component salts at 80°, varied greatly in composition; in no case did they correspond, even approximately, to

the formula given by Vohl, and they could only be represented by a formula by assigning to it a degree of complexity comparable with the errors of analysis. At the same time, there was evidence that these crystals could not be regarded as mere mixtures, for the dichroism exhibited by them showed that the composition of each was uniform throughout.

XV.—*The Influence of Silicon on the Properties of Cast Iron.* Part III.

By Thomas Turner, Assoc. R.S.M., Demonstrator of Chemistry, Mason College, Birmingham.

In the two former parts of this paper, an account has been given of a series of experiments undertaken with the view of determining the influence of silicon on cast iron. The results obtained were, in some respects, contrary to what might have been anticipated from the evidence on this subject which was previously in our possession. It became of considerable interest therefore, to ascertain whether these results were supported, or otherwise, by the work of other investigators; and whether, on the large scale, the same effects could be produced as had been noticed in these experiments conducted with but a few pounds of metal in the laboratory.

The chemistry of iron manufacture, as befits its great practical importance, has received much attention; and in the list of workers in this field may be found the names of many of our most illustrious chemists and engineers. But it would appear that the importance of combined chemical and mechanical testing has only of late years been fully recognised. Thus in the earlier experiments on the strength of cast iron, conducted upwards of half a century ago, the object appeared to be simply the determination of the limits of strength, and of the general average of a large number of specimens. This class of tests is doubtless of considerable value to the engineer, but to the chemist it is almost worthless. An advance was made some 40 years ago in the very important experiments of Fairbairn and Hodgkinson, by whom a large number of hot and cold blast irons were compared, and tests made upon iron of different grades from the same locality. This work entailed years of skilful, patient labour, and the results were of immense importance; but it is to be regretted that they were not accompanied by chemical analyses. The iron produced in any given locality often changes very much from time to time,

varying even in the same furnace from day to day; and we have no reason to suppose that the results obtained from an iron of certain locality and grade in 1844 would be of any importance as a guide to-day. If, however, analyses had been given, we should then have a standard for comparison much more permanent and important than that furnished by mere locality, and the value of such information to the practical chemist could scarcely be over estimated.

A great advance was attempted about 30 years ago in the work of the American Commissioners on the strength and other properties of metals for cannon, whose report appeared in 1856. In this report, chemical analyses accompanied the mechanical tests, and much benefit was anticipated from this combination. The mechanical tests afford considerable support to my own conclusions, especially in regard to tensile strength and hardness. In the best specimens examined, the observed tensile strength considerably exceeded the maximum found in my experiments, and which has been objected to in some quarters as being exceptionally high. The range of hardness also appears to fairly correspond with my own observations. In the case of their chemical analyses, however, the experimenters appear to have been less fortunate. Three chemical reports were issued, and in the last or "Final Report on Chemical Analyses," p. 394, we read:—

"Upon a comparison of this table with those heretofore presented during the progress of our researches, it will be observed . . . that the figures obtained by us for a few samples are discordant with those in the former tables. We are not aware how these errors may have occurred, but that they do exist is sufficient motive for our rejection of *all* the results, for where a few are wrong, all may justly be suspected."

The following examples will sufficiently illustrate the character of the discrepancy.

	No. 28 C.F. 42-pr. Specific gravity, 7·220 Tensile strength, 31,734 lbs.		No. 10 W.P.F. 32-pr. Specific gravity, 7·245 Tensile strength, 31,734 lbs.	
	2nd Report, p. 385.	3rd Report, p. 396.	2nd Report, p. 385.	3rd Report, p. 396.
Allotropic carbon	2·20	2·20	2·00	2·00
Combined carbon	1·70	1·70	2·22	2·22
Silicium	0·329	0·329	0·776	0·776
Slag	0·000	trace	0·25	0·25
Sulphur	0·033	—	—	—
Phosphorus............	10·31	0·436	1·09	0·036
Manganese	1·67	3·547	1·50	2·100

Though these results have been largely quoted in certain text-books, I have considered it best, under the circumstances, to imitate the example of the authors themselves, and not to draw any conclusions from unsatisfactory data.

In 1856 a most valuable series of experiments was commenced at Woolwich, and the results obtained are published in the report, "Cast Iron Experiments, 1858." This report probably contains the most complete information on British cast iron which we at present possess. As comparatively little systematic work has been done in this direction since the report was issued, it is worthy of more than passing attention; I propose therefore to examine the results in detail, in order, if possible, to show the influence exerted by silicon on the properties of the metal.

The chemical examination in these experiments was directed by Sir Frederick Abel, almost the whole of the analyses being performed by Mr. John Spiller; and on the most critical examination the work appears to be in every way worthy of the department by which it was conducted.

In this report, 70 different irons were examined, seven of which were of foreign origin. In most cases, determinations of the important chemical constituents are given, while an elaborate series of mechanical tests is also recorded. Analyses of ores and fluxes were performed in many cases, but with these we are not now concerned. For details as to the methods adopted, the shape and size of the test pieces, and other similar information, the report itself must be consulted, for in this place we shall be able only to deal with a short summary of the results. It is to be regretted, however, that the shape of the test pieces adopted for the determination of tensile strength, was not suitable for the accurate measurement of elongation; this fact is noticed in the report itself (p. 9), and has prevented my calculating the modulus of elasticity, which would otherwise have been of great interest, on account of the exceptional values obtained in some of my own experiments (comp. this Journal, Trans., 1885, 580 and 583).

In looking over the report and appendix, it will be found, that of the 70 irons experimented upon, eight are mentioned as being "too hard to turn." These are given in the following list (Table F, p. 133).

It will be noticed that in seven cases special hardness is accompanied by a low percentage of silicon; while in the mottled iron, where the silicon is present in sufficient quantity to produce very soft metal in a fairly pure iron, there is upwards of 1 per cent. of phosphorus, and this would quite account for its unusual hardness. This specimen is also richer in sulphur than any other iron examined in these experiments, this also would account for its greater hardness. These results

TABLE F.—*Iron too Hard to Turn.*

Locality, &c.	Silicon.	Phosphorus.
I. British Irons.		
Netherton, No. 5 strong forge	0·57	0·29
Ulverstone	0·59	0·10
Wellingborough, No. 2 mottled	2·11	1·07
II. Foreign Irons.		
Nova Scotia, white	0·21	1·53
Indian charcoal	0·44	0·27
Elba	0 71	0·07
Swedish grey	0·86	0·10
Tuscan	0·88	0·09

afford the strongest possible confirmation of the softening effect produced by a certain amount of silicon; an effect, so far as I am aware, first pointed out in my own experiments. Hitherto it has been the general custom to attribute an entirely opposite influence to this element.

The seven foreign irons mentioned in the appendix form a very interesting series, when arranged in order of silicon (Table G).

TABLE G.—*Foreign Irons (Arranged in Order of Silicon).*

No.	Locality, &c.	Chemical analysis.						Transverse strength.	Working qualities.
		Mn.	Si.	Graphite.	Combined C.	S.	P.		
1	Nova Scotia white	—	0·21	—	2·96	0·02	1·53	4141	Too hard to turn.
2	Indian charcoal	0·14	0·44	3·38	—	0·04	0·27	4120	Too hard to turn.
3	Elba	—	0·71	3·08	—	0·03	0·07	4249	Too hard to turn.
4	Swedish grey	0·17	0·86	3·21	—	0·03	0·10	5673	Too hard to turn.
5	Tuscan	trace	0·88	2·91	—	0·08	0·09	3934	Too hard to turn.
6	Nova Scotia grey	0·25	1·11	3·29	—	0·01	0·13	8092	Good and soft.
7	New York, sterling	0·08	1·33	2·87	—	0·02	0·09	8210	Good and soft.

This list contains *all* the foreign irons mentioned in the report, and very well illustrates the effect of silicon on the tenacity and working qualities of cast iron, entirely confirming the results of my own experiments. It will be seen that the first five specimens are too low in silicon, and are consequently inferior both in strength and working qualities; while even the two last, which contain most silicon, and are the best irons in the series, do not quite reach the best proportion as deduced from my observations. The transverse test was the only one which could be applied in the first five specimens, poor in silicon, owing to their great hardness.

We will now take a general survey of the results given in the report, as distinguished from the appendix, with the object of making clear the influence of silicon on the mechanical properties of the metal. This part includes 53 samples, two of which were too hard to turn, and in which the mechanical tests were consequently incomplete. In one other case, the analysis is not given. Hence in each series of tests we have 51 to 53 samples, and these are arranged in the report in order of quality. It will be obvious that in such a case the average order of quality of the whole series would be about 26. Any specimen in the list above this number may be considered as of more than ordinary quality, while those below 26 are of inferior quality. For comparison I have selected three sets, each containing six specimens, viz., the six *lowest* in silicon, the six *best* specimens, and the six *highest* in silicon. The analyses are given side by side with the order of quality in sp. gr., and tensile, transverse, torsional, and crushing strengths; for these latter a mean is obtained, and a general average is deduced for each series (see Table H, p. 135). The results are as follows:—

	Average Si per cent.	Average order of quality.
Six specimens lowest in silicon......	0·983	16·0
Six best specimens................	1·393	6·4
Six specimens highest in silicon	3·48	42·3

These numbers show conclusively that the specimens *lowest* in silicon are not the best. It is true that they are above the average in order of quality—we have seen the general average is about 26—but this is accounted for by the fact that no white irons were examined, and so the amount of silicon present is not *much* below the most suitable proportion for general strength. The six best specimens contain, on an average, 1·393 per cent. of silicon; and it will be remembered that my own experiments showed the most suitable amount to be about 1·4 per cent., so that the agreement is remarkably good. In the six specimens highest in silicon, the ill effects of too large a proportion is very marked.

TABLE H.—From "Cast Iron Experiments, 1858," pp. 154–5.

I. *Six Specimens with Lowest Silicon (in Order of Silicon).*

No.	By whom supplied.	Description.	Chemical analysis.					Order of quality.					Mean.	Working qualities.	Remarks.
			Mn.	Si.	Graphite.	S.	P.	Specific gravity.	Tensile.	Transverse.	Torsion.	Crushing.			
1	Blaenavon Iron Works.........	No. 1 and C forge	0·53	0·31	2·82	0·06	0·38	18	10	9	40	13	18·0	Good	
2	Netherton Iron Works	No. 4 and 5 forge	0·27	0·83	3·03	0·04	0·31	5	3	1	5	10	4·8	,,	
3	Park Head, Dudley	Foundry melting pig...	0·55	0·96	2·89	0·06	0·58	9	9	15	8	19	12·0	Very good	
4	Lays Works, Dudley............	Hæmatite iron	1·14	1·05	3·15	0·05	0·29	2	1	6	43*	6	11·6	Good	*Faulty specimen.
5	Blaenavon Iron Works.........	No. 3 cold blast	0·66	1·09	2·88	0·03	0·38	20	25	20	36	28	25·8	Inclined to be soft	
6	Netherton Iron Works	No. 3 grey forge.........	0·94	1·16	3·12	0·05	0·44	19	23	19	24	35	24·0	Good	

Average per cent. silicon = 0·983. Average order of quality = 16.

II. *Six best Specimens in the Series (in Order of Quality).*

No.	By whom supplied.	Description.	Mn.	Si.	Graphite.	S.	P.	Specific gravity.	Tensile.	Transverse.	Torsion.	Crushing.	Mean.	Working qualities.	Remarks.
1	West Hallam, Derbyshire ...	No. 3 melting pig	0·45	1·26	2·60	0·05	0·72	4	5	2	2	4	3·4	Good	
2	,, ,, ,,	No. 2 melting pig	0·60	1·50	2·40	0·06	0·34	6	6	3	1	7	4·6	,,	
3	Netherton Iron Works.........	No. 4 and 5 forge	0·27	0·83	3·03	0·04	0·31	5	3	1	5	10	4·8	,,	Classed above.
4	Park Head, Dudley	Forge	0·86	1·21	3·00	0·10	0·48	10	2	5	4	11	6·4	,,	
5	Weardale Iron Co...............	Remelted	0·13	1·88	2·21	0·10	0·19	12	4	4	21	3	8·8	,,	
6	Blaenavon Iron Works.........	Common forge...........	0·66	1·68	2·64	0·08	0·27	1	7	12	30*	1	10·2	Very difficult	*Faulty specimen.

Average per cent. silicon = 1·393. Average order of quality = 6·4.

III. *Six Specimens with Highest Silicon (in Order of Silicon).*

No.	By whom supplied.	Description.	Mn.	Si.	Graphite.	S.	P.	Specific gravity.	Tensile.	Transverse.	Torsion.	Crushing.	Mean.	Working qualities.	Remarks.
1	South Bank, Middlesbro'	No. 2 foundry pig	0·38	2·73	3·04	0·04	1·30	49	47	47	38	40	44·2	Good	
2	Hæmatite, Whitehaven........	No. 3 foundry pig	0·07	2·77	2·24	0·01	0·05	7	44	50	48	36	37·0	,,	
3	,, ,,	No. 1 foundry pig	0·11	3·02	3·22	0·00	0·06	40	49	52	51	50	48·4	,,	
4	Weardale Iron Co.............	No. 3 pig-iron	1·04	4·25	2·26	0·06	0·07	21	35	25	29	23	26·6	,,	
5	Old Hill, Dudley.................	No. 2 foundry pig	0·30	3·48	3·06	0·03	0·38	50	48	49	46	51	48·8	,,	
6	Heyford Works, Weedon.. ...	Pig-iron, first melting.	trace	4·63	2·64	0·07	1·31	51	51	53	49	41	49·0	Difficult	

Average per cent. silicon = 3·48. Average order of quality = 42·3.

Note.—When taking the six lowest in order of silicon, "South Bank, Middlesbro', toughened pig" is excluded, as it contained as much as 1·24 per cent. P. and 1·13 per cent. Si. Its average order of quality = 34·2.

But however conclusive such a general view as the above at first appears, it might be supposed that a closer examination of the report would not support the conclusions drawn. We shall, therefore, proceed to consider the report in detail, and to examine the results obtained in each specimen examined. Such a task is one of no small difficulty, and a number of irregularities must be confidently anticipated. These are due in great part to the fact that we have to do with at least six variables, namely, manganese, silicon, graphitic and combined carbon, sulphur, and phosphorus. Each of these substances exerts a considerable influence on the character of the product, and we have little knowledge of a definite character as to the influence of different proportions of these elements, either alone or in presence of each other, on cast iron. Added to this, we have the errors due to experimental observation, both chemical and mechanical, which in several hundreds of analyses, and a much larger number of mechanical tests, must be by no means inconsiderable. In many cases also the differences in silicon are but small, sometimes less than 0·1 per cent., so that its effect is entirely overcome by variations in other elements present. Lastly, it would appear that the analyses were made on the samples *as received*, which was probably the best way under the circumstances; but the result is, that they do not accurately represent the composition of the actual pieces tested, owing to slight alteration during melting; this introduces a considerable disturbing influence when the composition of the metal is very nearly the same in several specimens. Hence, if we are successful in showing the general influence, and in accounting for most of the important exceptions, we shall accomplish all that can be reasonably anticipated.

In order to eliminate, as far as possible, one source of variation, and to reduce the number of specimens to be compared together at one time, I have divided the results according to the amount of phosphorus present. It would be obviously unfair to compare together two specimens differing from each other by less than 0·1 per cent. of silicon, and by over 1 per cent. of phosphorus, as the influence of a small variation of silicon would be entirely masked by the large variation in phosphorus.

I. *Non-phosphoric Pig-iron.*

Beginning in order, we take first non-phosphoric pig-iron. In the report we have nine specimens, each containing under 0·20 per cent. of phosphorus; these are arranged, in order of silicon, in Table K. It will be seen that all the specimens possessed good working qualities, except the first, which was the lowest silicon and highest sulphur

TABLE K.—*Non-phosphoric Pig-iron (under 0·2 per cent.) in Order of Silicon.*

No.	By whom supplied.	Description.	Chemical analysis.					Order of quality.					Mean.	Working qualities.	Remarks.
			Mn.	Si.	Graphite.	S.	P.	Specific gravity.	Tensile.	Transverse.	Torsion.	Crushing.			
1	Weardale Iron Co.	No. 4 pig-iron	trace	1·18	2·15	0·12	0·19	3	28	17	19	9	15·2	Tolerable	
2	,, ,,	No. 1 pig-iron	1·45	1·80	3·24	0·04	0·19	43	43	46	39	48	43·8	Good	Mn. high.
3	,, ,,	Remelted	0·13	1·88	2·21	0·10	0·19	12	4	4	21	3	8·8	,,	
4	Park End Furnaces, Gloster	Grey forge	0·14	2·18	3·03	0·06	0·14	13	46	37	23	46	33·0	,,	
5	,, ,, ,,	Foundry pig	0·23	2·34	3·26	0·04	0·14	38	50	48	47	49	46·4	Good and soft	
6	Hæmatite, Whitehaven	No. 4 foundry pig	0·07	2·63	1·86	0·10	0·03	8	45	42	45	34	34·8	Good	Total C. = 2·21.
7	,, ,,	No. 3 foundry pig	0·07	2·77	2·24	0·01	0·05	7	44	50	48	36	37 0	,,	
8	,, ,,	No. 1 foundry pig	0·11	3·02	3·22	0·00	0·06	40	49	52	51	50	48·4	Good and soft	
9	Weardale Iron Co.	No. 3 pig-iron	1·04	4·25	2·26	0·06	0·07	21	35	25	29	23	26·6	Good	Mn. high.

TABLE L.—*Slightly Phosphoric Pig-iron (0·2 to 0·4 per cent.) in Order of Silicon.*

No.	By whom supplied.	Description.	Chemical analysis.					Order of quality.					Mean.	Working qualities.	Remarks.
			Mn.	Si.	Graphite.	S.	P.	Specific gravity.	Tensile.	Transverse.	Torsion.	Crushing.			
1	Blaenavon	No. 1 and C forge	0·53	0·81	2·82	0·06	0·38	18	10	9	40	13	18·0	Good	
2	Netherton, Dudley	No. 4 and 5 forge	0·27	0·83	3·03	0·04	0·31	5	3	1	5	10	4·8	,,	
3	Lays Works, near Dudley	Hæmatite, 1st melting	1·14	1·05	3·15	0·05	0·29	2	1	6	43	6	11·3	,,	
4	Blaenavon	No. 3 cold blast	0·66	1·09	2·88	0·08	0·38	20	25	20	36	28	25·8	Inclined to be soft	
5	Netherton, Dudley	No. 2 foundry pig	0·80	1·27	3·04	0·04	0·34	14	14	7	9	32	15·2	Good	
6	Blaenavon	No. 1 cold blast	0·28	1·36	3·40	0·07	0·29	30	17	23	44	20	26·8	Inclined to be soft	Highest graphite.
7	Pontypool	Cold blast	0·42	1·46	2·42	0·12	0·32	15	12	39	42	15	24·6	Good	Highest sulphur.
8	West Hallam, Derbyshire	No. 2 melting pig	0·60	1·50	2·40	0·06	0·34	6	6	3	1	7	4·6	,,	
9	Ystalyfera	No. 3 foundry, 1st	0·43	1·55	3·16	0·06	0·27	23	27	14	12	33	21·8	,,	
10	Blaenavon	Common forge	0·66	1·68	2·64	0·08	0·27	1	7	12	30	1	10·2	Very difficult	
11	Ystalyfera	No. 3 foundry, 2nd	0·27	1·71	2·61	0·05	0·38	24	22	28	35	24	26·6	Good	
12	,,	No. 2 foundry, 2nd	0·39	1·73	2·92	0·06	0·29	22	11	10	25	22	18·0	,,	
13	,,	No. 2 foundry, 1st	0·14	2·07	2·55	0·09	0·38	32	36	29	15	42	30·8	,,	
14	Old Hill, Dudley	No. 2 foundry	0·30	3·48	3·06	0·03	0·38	50	48	49	46	51	48·8	,,	

of the series. On examining the average order of quality, we find that there is a marked resemblance to my own results, but three specimens are a little exceptional, being in two cases inferior to what might have been anticipated from their silicon content (Nos. 2 and 5), while in the other case (No. 9) the quality is improved. The first named two specimens are highest in graphite, and this accounts for their weaker character, as an addition of but a few tenths per cent. of graphite beyond 3 per cent. appears to weaken the iron very much. In No. 9 a low proportion of graphite and over 1 per cent. of manganese appears to have partly neutralised the bad effects of 4·25 per cent. of silicon. On allowing for these differences of chemical composition, we find that the series shows an improvement on adding silicon up to 1·88 per cent., and then gradually deteriorates with a greater proportion. This effect is exactly similar to that seen in my own experiments, except that in the present instance it is somewhat obscured by variations of other elements present.

II. *Slightly Phosphoric Pig-iron.*

Passing now to material containing a little more phosphorus, we find that there are 14 specimens mentioned in the report which contain from 0·2 to 0·4 per cent. of phosphorus. These are arranged, just as before, in order of silicon (see Table L, p. 137), and they exhibit less variation due to silicon than any other class of iron mentioned in the report. The reasons for this are very apparent on careful examination.

The two last specimens in the list have been separated from the others by a line, because in these two cases it is evident that too large a proportion of silicon is present, and the metal is weakened in consequence, as shown by the low average order of quality. The proportion, however, is not sufficient to interfere with the working qualities. But on examination of the other 12 specimens it will be found that the *maximum* difference in silicon is only 0·92 per cent., which gives an average difference between two adjacent specimens of only about 0·08 per cent. of silicon. But it will be noticed that in the same specimens the graphite varies by 1 per cent., and manganese by 0·87 per cent., while the sulphur and phosphorus also introduce some irregularity. When we further remember liability of experimental error, the fact that the analyses were made before remelting, and the very rigid character of the test we are applying, it is not to be wondered at if the results are irregular. In this series of 12 specimens, we find that the effect produced by variations of silicon is counterbalanced by the considerable and irregular alterations of the proportion of other elements present. The highest and lowest specimens are

almost equally removed from 1·4 per cent., and are of exactly the same average order of quality; while the mean order of quality of the first six specimens is 17, and of the last six specimens 17·6, or almost exactly the same. From these results we may conclude that within the range of ± 0·5 per cent. from 1·4 per cent. of silicon, irons are of good average, or very superior quality, but that their relative quality is liable to be much influenced by other comparatively small differences in composition.

III. *Moderately Phosphoric Pig-iron.*

In this class are included all irons containing from 0·4 to 1 per cent. of phosphorus; and for sake of convenience they are divided into two series.

A. *Containing* 0·4 *to* 0·6 *per cent.*—Of these there are nine given in the report, and they are arranged in order of silicon in Table M (p. 140). In this series we have only a difference of 0·91 per cent. of silicon, while manganese varies by 0·96 per cent., and hence introduces a disturbing effect. But as each specimen which contains much manganese is deteriorated in quality thereby, its effect may be plainly observed. On making suitable allowance for these cases, we find the effect is quite similar to that noticed in Table K (p. 137), and also in my own experiments.

B. *Containing* 0·6 *to* 1 *per cent.*—Of these there are eight given in the report, and we have them arranged in order of silicon in Table N (p. 140). It will be seen that Nos. 2, 3, 4, 7, and 8 form part of a regular series, resembling those noticed in Tables K and M. But there are three exceptions to the regular order. Of these No. 5 is the highest manganese of the series, and is consequently of inferior quality; and No. 6 is slightly inferior, though in this case the reason is not so plain. No. 1 is also out of order, and at first sight it appears to be so to a serious degree, as this is the best specimen examined in the whole of the experiments recorded in the report. But when we notice that an increase of less than 0·2 per cent. of silicon would cause it to take what we may assume to be its proper place in the series, it will be seen how very close the general agreement must be.

IV. *Phosphoric Pig-iron.*

In this class we include all specimens containing upwards of 1 per cent. of phosphorus; of these there are 10 given in the report. They are arranged in order of silicon in Table O (p. 141), and strikingly exhibit the effect we have previously noted in the other series. The specimens highest and lowest in silicon are both inferior, while the best

TABLE M.—*Moderately Phosphoric Pig-iron (0·4 to 0·6 per cent.) in Order of Silicon.*

No.	By whom supplied.	Description.	Chemical analysis.					Order of quality.					Mean.	Working qualities.	Remarks.
			Mn.	Si.	Graphite.	S.	P.	Specific gravity.	Tensile.	Transverse.	Tor-ion.	Crushing.			
1	Park Head, Dudley	Foundry pig	0·55	0·96	2·89	0·06	0·58	9	9	15	8	19	12·0	Very good	
2	Netherton, Dudley	No. 3 grey forge	0·94	1·16	3·12	0·05	0·44	19	23	19	24	35	24·0	Good	Mn. and graphite high.
3	Park Head, Dudley	Forge	0·86	1·21	3·00	0·10	0·48	10	2	5	4	11	6·4	,,	
4	Old Hill, Dudley	Strong forge	0·54	1·36	2·55	0·11	0·41	27	8	13	33	5	17·2	Tolerable	
5	Netherton. Dudley	No. 1 foundry	0·96	1·48	3·07	0·03	0·43	35	37	33	26	45	35·2	Good	Mn. high.
6	Ystalyfera	No. 1 foundry, 1st	0·32	1·58	3·17	0·05	0·42	33	20	18	22	26	23·8	,,	
7	Park Head, Dudley	Grey forge	0·95	1·63	2·90	0·03	0·55	44	41	44	28	47	40·8	,,	Mn. high.
8	Old Hill, Dudley	No. 4 forge	trace	1·75	2·76	0·07	0·55	47	32	35	34	39	37·4	,,	
9	Ystalyfera	No. 1 foundry, 2nd	0·27	1·87	3·27	0·05	0·41	17	21	11	14	27	18·0	,,	

TABLE N.—*Moderately Phosphoric Pig-iron (0·6 to 1 per cent.) in Order of Silicon.*

No.	By whom supplied.	Description.	Chemical analysis.					Order of quality.					Mean.	Working qualities.	Remarks.
			Mn.	Si.	Graphite.	S.	P.	Specific gravity.	Tensile.	Transverse.	Torsion.	Crushing.			
1	West Hallam, Derbyshire	No. 3 melting pig	0·45	1·26	2·60	0·05	0·72	4	5	2	2	4	3·4	Good	
2	Butterley, Derbyshire	No. 3 blue rake	0·40	1·34	2·60	0·11	0·75	46	24	26	18	18	26·4	Tolerable	
3	Level Works, Brierley Hill	Hot blast	0·49	1·40	2·61	0·04	0·72	28	13	27	31	14	22·6	Good	
4	West Hallam, Derbyshire	Grey forge	0·89	1·41	2·74	0·03	0·95	16	19	16	3	17	14·2	,,	
5	,, ,, ,,	No. 4 strong forge	0·94	1·53	2·57	0·05	0·70	37	39	30	17	43	33·2	,,	Mn. high.
6	Level Works, Brierley Hill	Cold blast	0·06	1·75	2·55	0·05	0·63	48	15	36	37	31	33·4	,,	
7	West Hallam, Derbyshire	No. 1 melting pig	0·88	2·23	2·31	0·02	0·72	36	34	22	7	37	27·2	,,	
8	Old Hill, near Dudley	No. 3 grey forge	0·34	2·24	2·69	0·04	0·69	39	26	24	10	38	27·4	Tolerable	

TABLE O.—*Phosphoric Pig-iron (over 1 per cent.) in Order of Silicon.*

No.	By whom supplied.	Description.	Chemical analysis.					Order of quality.					Mean.	Working qualities.	Remarks.
			Mn.	Si.	Graphite.	S.	P.	Specific gravity.	Tensile.	Transverse.	Torsion.	Crushing.			
1	South Bank, Middlesbro'	No. 2 toughened	0·43	1·13	3·44	0·03	1·24	42	42	41	16	30	34·2	Tolerable	
2	Butterley, Derbyshire..........	No. 1 foundry...........	1·01	1·27	3·35	0·02	1·09	29	29	32	6	25	24·2	Good	Graphite high. P. low.
3	Stockton Iron Works...........	No. 3 hot blast...........	0·06	1·43	3·31	0·03	1·36	31	33	34	20	29	29·4	Tolerable	
4	,, ,, ,, ...	No. 1 hot blast.....	0·07	1·57	3·35	0·04	1·38	26	16	31	32	16	24·2	,,	
5	Butterley, Derbyshire..........	No. 3 foundry............	0·95	1·75	2·71	0·04	1·15	34	30	38	11	21	26·8	Good	
6	East End, Wellingbro'	No. 1 grey..................	0·24	1·92	2·85	0·10	1·19	11	38	45	41	12	29·4	Difficult	
7	Butterley, Derbyshire..........	No. 2 foundry............	1·06	2·36	2·74	0·02	1·21	45	40	43	27	44	39·8	Good	
8	Goldendale, N. Stafford........	Pig-iron	0·93	2·71	2·54	0·04	1·07	41	18	21	13	51	20·2	Tolerable	Lowest graphite and P. of series.
9	South Bank, Middlesbro'......	No. 2 foundry	0·38	2·73	3·04	0·04	1·30	49	47	47	38	40	44·2	Good	
10	Heyford, near Weedon.........	Pig, first melting........	trace	4·63	2·64	0·07	1·31	51	51	53	49	41	49·0	Difficult	

specimen contains 1·57 per cent., and agrees remarkably with the recommendation of Mr. Wood for Cleveland iron, which is of a similar character to the iron in this series. In a note incorporated in my previous paper (Trans., 1885, 913), Mr. Wood recommended 1·5 to 1·75 per cent. of silicon for production of strong foundry iron from Middlesbrough pig. In Table O (p. 141), there are two specimens which are slightly irregular (Nos. 2 and 8), each of them being of rather superior average quality. This is explained by the fact that they contain the least phosphorus in the series; and also that in No. 2, where silicon is low, graphite is high; whilst in No. 8, where silicon is high, we have the lowest graphite of the series. These facts are quite sufficient to explain the slight irregularity noticed, and the series is then of remarkable uniformity.

We have now come to the end of the report itself, which dealt with 53 specimens; 50 of these we have considered; 2 were too hard to turn, and have been previously mentioned; whilst in the remaining case no analysis was given. In the appendix, 17 specimens are mentioned, 7 of which are foreign irons, and are given in Table F, p. 133; 2 were prepared by patent processes, and these are not sufficiently numerous for comparison; whilst of the remaining 8 we have only 6 analyses. The results of these are given in Table P, the specimens being arranged, as usual, in order of silicon.

In these experiments, the manganese was not determined, and the mechanical tests were also incomplete, but the same kind of effect is noticed as in my own experiments, the best results being obtained with a moderate amount of silicon. The very sudden decrease in

TABLE P.—*English Irons.*

Locality, &c.	Analysis.					Tensile.	Transverse.	Remarks.
	Mn.	Si.	Graphite.	S.	P.			
1. Ulverstone ...	—	0·59	2·83	0·03	0·10	17,592	5,541	Too hard to turn.
2. Bowling.....	—	0·97	2·99	0·05	0·50	27,367	9,740	
3. Bowling, No. 2, 2nd sample..	—	1·01	2·98	0·03	0·49	26,821	8,999	
4. Bowling, No. 3, 2nd sample..	—	1·03	2·84	0·04	0·52	29,344	10,016	
5. Bowling, No. 2, 1st sample ..	—	1·08	3·32	0·06	0·56	15,600	6,347	
6. Bowling, No. 3, 1st sample ..	—	1·71	3·14	0·07	0·67	17,530	5,012	

tensile strength noticed in No. 5 is probably connected with the large proportion of graphite present.

We have now considered every specimen mentioned in this most valuable report, and my endeavour has been to bring forward the evidence in such a manner that all who are interested may be able to judge of the validity of my conclusions. My friend Mr. John Spiller allows me to mention that he has carefully gone over my tables, and considers that in their preparation the report has been honestly dealt with, and, in the main, he coincides with my conclusions.

Sir W. Fairbairn's Experiments.—In the Report of the British Association for 1853, an account is given of some experiments by Sir (then Mr.) W. Fairbairn, undertaken to ascertain the effect of repeated meltings on the properties of cast iron. As this question is one of very considerable practical importance, I shall venture to deal with these experiments in detail. The results have been often quoted by different writers, and the mechanical tests appear to have been very careful and complete, although it is to be regretted that the chemical analyses were not so fully performed. In Table Q (p. 144) is given a summary of the most important results obtained; and in addition to what is included in the report, I have added the calculated tensile strength from Box's "Strength of Materials," and also the *probable* amounts of silicon, sulphur, and carbon contained in the best specimen, as calculated from the other analyses given, and the average rate of change of composition.

The iron used was Eglinton No. 3, hot blast, which was remelted 18 times. We cannot here enter into details as to the shape of test pieces, and method of operation; but it will be seen from Table Q the metal was at first slightly deteriorated by remelting, that afterwards it was much improved, reaching a maximum at the twelfth fusion, but on further melting it again deteriorated, and became very inferior indeed after the fifteenth fusion.

These effects have generally been attributed to remelting, as if there were some particular charm in the process of fusion capable of improving the quality of the product. But Dr. Percy, in speaking of these experiments says, "As fusion was effected in a cupola (comp. note, p. 147) with coke as the fuel, it is obvious that in the course of remelting the iron might have suffered important chemical changes in composition, which may greatly modify its properties. It is hardly conceivable that *simple melting*, without the addition of anything to, or the subtraction of anything from the metal, should produce any decided effect." ("Iron and Steel," p. 862.)

Dr. Percy's suggestion of "important chemical changes," during remelting, is fully borne out by an examination of Table Q (next page). It will be seen that silicon increases from 0·77 to 2·22 per cent., the

TABLE Q.—*The Effect of repeated Meltings on the Mechanical Properties of Cast Iron* (British Assoc. Report, 1853, p. 87).

No. of meltings.	Percentage of Si.	Percentage of S.	Percentage of C.	Specific gravity.	Mean breaking weight in lbs. per sq. in.	Mean ultimate deflection in inches.	Power to resist impact.	Resistance to compression. Tons per sq. in.	Calculated* tensile strength. Tons per sq. in.	Remarks.
1	0·77	0·42	2·76	6·969	490·0	1·440	705·6	44·0	9·507	Close grained, very uniform in texture.
2	—	—	—	6·970	441·9	1·446	630·9	43·6	8·217	Nearly the same in every respect.
3	—	—	—	6·886	401·6	1·486	596·7	41·1	7·351	Less lustre, otherwise the same.
4	—	—	—	6·938	413·4	1·260	520·8	40·7	7·697	Metal harder, colour as before.
5	—	—	—	6·842	431·6	1·503	648·6	41·1	8·151	More lustre; bluish; interior crystals larger.
6	—	—	—	6·771	438·7	1·320	579·0	41·1	8·349	Metal soft; appearance the same.
7	—	—	—	6·879	449·1	1·440	646·6	40·9	8·655	Density and hardness increased.
8	1·75	0·60	2·30	7·025	491·3	1·753	861·2	41·1	9·847	Colour and form as before.
9	—	—	—	7·102	546·5	1·620	885·3	55·1	10·07	More uniform and compact, colour same.
10	1·98	0·26	3·50	7·108	566·9	1·626	921·7	57·7	10·40	Firm grain, rather hard, perfectly uniform.
11	—	—	—	7·113	651·9	1·636	1066·5	69·8	11·71	Rather lighter colour, otherwise the same.
12	(2·04)†	(0·38)†	(3·54)†	7·160	692·1	1·666	1153·0	73·1	12·51	Strong finely grained texture; light grey.
13	—	—	—	7·134	634·8	1·646	1044·9	66·0 (too low)	11·54	Strong close grained iron, with sharp angular crystals.
14	—	—	—	7·530	603·4	1·513	912·9	95·9	9·154	Close grained grey; somewhat hard and brittle.
15	—	—	—	7·248	371·1	0·643	238·6	76·7	5·366	Light grey in centre; *silvery white* at each corner.
16	—	—	—	7·330	351·3	0·566	198·5	70·5	5·116	Silvery white, except ¼″ in centre; very hard.
17	The 17th melting was a failure, the iron being too stiff to run into bars.									
18	2·22	0·75	3·75	7·385	312·7	0·476	148·8	88·0	4·196	White and silvery over the whole surface.

* The calculated tensile strength is taken from T. Box, "Strength of Materials," p. 10.

† Probable composition.

increase appearing to be of a fairly uniform character. The amount of sulphur varies irregularly from 0·26 to 0·75 per cent.; while the proportion of carbon varies, not very regularly, from 2·3 to 3·75 per cent.

Under these circumstances it is evident that the chemical changes are amply sufficient to account for the effect produced, quite apart from any change due to remelting simply. In order to make this clear, the table is divided into three parts by horizontal lines, and these parts we will consider in order.

1. The three first meltings produced a deterioration in the properties of the metal. The cause of this cannot be ascertained with certainty, as we have no analysis at the end of the third melting. But it is quite possible that the increase of sulphur, of which we find evidence in the next analysis, took place about here, the sulphur being derived from the coke employed.

2. In the 11 following meltings, we find the sulphur and carbon somewhat irregular, but silicon appears to have been added slowly and with considerable regularity, and its effect is seen to be exactly the same as in the experiments to which previous reference has been made, including the Woolwich experiments, Mr. Wood's recent work, and those I have given in Parts I and II of the present paper. In this case, the influence on the mechanical properties of the metal is very regular and well marked, the maximum improvement being produced by about 2 per cent. of silicon. This amount is a little greater than that found in the other experiments, but the iron operated on contained more sulphur than in any previous case; and as sulphur and silicon, in due proportion, appear to have almost opposite effects, it would be naturally expected that the most suitable proportion of silicon would be higher than usual.

3. In the four last meltings, the quality is very inferior: the most suitable proportion of silicon has now been exceeded, as we saw previously; but it would be quite unfair to attribute the whole of the sudden decline in quality to this cause. It will be seen that the last melting contained no less than 0·75 per cent. of sulphur, while the tenth melting had only 0·26 per cent. A careful consideration of the properties of the metal will show that sulphur considerably increased about the fourteenth and fifteenth meltings, rendering the metal hard, white, and brittle; and these changes were accompanied by a very sudden decrease in strength.

It will be seen from this brief survey, that the effect attributed to remelting may be sufficiently explained by a consideration of the chemical changes which took place. It may be added that these results are quite inexplicable on the supposition that "silicon is always bad;" but on the other hand, when due allowance is made for

the disturbing influence exerted by sulphur, they afford strong confirmation of my own results.

It is not contended that remelting, when unaccompanied by chemical change, is never beneficial. It is well known that castings made directly from the blast furnace are unsatisfactory, and in this case probably the iron would be improved by remelting, even if it *could* be accomplished without chemical change, as it would ensure greater uniformity in the metal. In this respect the common practice of casting from a cupola, especially with suitable mixtures of iron, is to be commended. But any attempt to further improve the quality by remelting is not wise. It has been shown that some metal is improved up to the twelfth melting; others to the eighth; some only to the fourth, whilst some cast iron is deteriorated by even one melting. This will obviously depend on the character of the metal and the changes which take place during remelting, such as alterations in silicon, sulphur, carbon, &c. It is evident that these changes may be produced more readily, and with greater certainty, by judicious mixing, than by the laborious and expensive process of remelting.

It was pointed out by Robert Mallet, so far back as 1856 ("Construction of Artillery," pp. 13 and 218), that the results obtained in Fairbairn's experiments did not depend upon remelting alone; but at that time our knowledge of the influence of the various constituents present in cast iron was insufficient to enable either Mallet or Percy to point out the precise reason for the changes, though they correctly indicated the directions whence the alterations proceeded.

In addition to the experiments to which I have previously referred, there are a number of other facts which strongly support the conclusions drawn from my own experiments as to the influence of silicon in cast iron. Among the more important of these may be mentioned Stirling's method for producing toughened cast iron, by mixing soft grey pig with wrought iron scrap in suitable proportion; Price and Nicholson's patent cast iron, produced by mixing white and grey iron in suitable quantities; and lastly, the more recent use, chiefly in America, of steel scrap as a means of strengthening cast iron. The advantage of these methods is undoubted in many cases, but it is not to be wondered at that unsatisfactory results were often obtained when silicon was regarded as being a noxious impurity under all circumstances. As a consequence, the proportion of silicon was often lowered in metal which already contained too little, with the result of rendering the iron both hard and weak. This part of the subject has a more practical bearing than the purely experimental part, and so will probably be considered more in detail elsewhere. But it may be added that in each of the cases mentioned the object aimed at was not

to produce a steel, but a cast iron of special quality, the carbon and silicon present being generally reduced by only one-eighth to one-fourth of the original amount.

On examining the various tables previously given, and selecting from each the specimen which apparently contained the most suitable proportion of silicon, we have the following result—

	Silicon, per cent.
1. English irons in the Appendix (Table P)	1·03
2. Containing 0·4 to 0·6 per cent. P. (Table M)..	1·21
3. Foreign irons in the Appendix (Table G)	1·33
4. Average of six best specimens (Table H)	1·39
5. Containing 0·6 to 1 per cent. P. (Table N)....	1·41
6. Containing over 1 per cent. P. (Table O)	1·57
7. Containing under 0·2 per cent. P. (Table K)..	1·88
8. Sir William Fairbairn's experiments (Table Q)	2·04 ?
Average	1·48

It will be seen that this average amount varies but little from that which I have previously suggested (1·4 per cent.) as the most suitable proportion for strong iron (Trans., **47**, 912). And, when discussing the results in detail, we have already seen the reasons which tended to make the amount somewhat irregular, where any considerable variation from the average is observed. For my own part, on considering the facts now brought forward, together with the results of Mr. Wood's work and my own experiments, I regard it as abundantly proved, that silicon, when present in suitable proportion, is a true friend to the iron-founder, since, with no extra expenditure, a stronger, softer, sounder iron may be produced.

In bringing my paper to a close, I would express my belief that by a knowledge of the constituents of the cast iron employed, and a suitable mixture of material to produce the best result, the average strength of cast iron in this country could be very considerably increased. At the same time good working qualities could be regularly obtained, while no extra cost in production need be incurred.

Note by the Author.—In the discussion which followed the reading of this paper (Abstracts of Proceedings, p. 135), it was mentioned by Professor Unwin, who took part in Sir William Fairbairn's experiments, that the remelting was performed in an air furnace, and not in a cupola, as stated in the extract from Dr. Percy given in the text. I am pleased to be able to make this correction, as it explains why so many meltings were possible before the metal suffered seriously in

properties. Not being able to find any record of the methods adopted for remelting, I naturally accepted the statement of so excellent an authority as Dr. Percy. Otherwise, however, my conclusions are unaffected by this slight error. The fact remains that important chemical changes occurred, and that these changes, which were probably gradual, are amply sufficient to account for the alterations in the character of the product, quite apart from any virtue in remelting *per se*. In the discussion it was stated that "the change in properties on remelting has always been attributed to the change from graphitic to combined carbon;" and remelting is commonly believed to produce this result. It may, however, be pointed out that remelting does not always increase the amount of combined carbon; it has occasionally an entirely opposite effect. Thus, under certain circumstances, white iron may be converted into grey by remelting, quite apart from any effect due to slow cooling. The probable causes for the belief that remelting hardens iron are two-fold. First, the fact that the fuel (coke) oftens contains a considerable proportion of sulphur; and secondly, as foundry iron is a soft grey, seldom containing more than 0·5 per cent. of combined carbon, we have practically only one kind of change possible, namely, a reduction of graphitic carbon, for obviously it cannot under these circumstances be increased.

It is not sufficient to say that the graphitic carbon is altered. We want to know *why* this is altered. It has yet to be proved that remelting, apart from chemical change, is capable of producing this effect. On the other hand, we do know that addition of silicon to a white iron produces grey iron, as shown in Part I; while the addition of sulphur to a grey iron produces a mottled or white product. Hence, when no other constituent is present in unusual quantity, we can predict with tolerable accuracy the relative proportion of graphitic to combined carbon in a sample of iron, when the proportions of silicon and sulphur are known. Now since for this prediction we do not require to know the number of times the iron has been remelted, but only the chemical analysis of the product, it is obvious that the alterations in the proportion of graphitic carbon are due to chemical changes and not to the mere operation of fusion.

It is for this reason that I have not referred to the proportion of carbon in Sir W. Fairbairn's experiments. It will be found that in the original paper mention is made of the unsatisfactory methods by which carbon was then estimated, and no distinction is made between graphitic and combined. But in the variations of sulphur and silicon we have an index to the variations in graphitic carbon; and in these experiments we have, as it were, a struggle for supremacy between sulphur and silicon. In the second portion of Table Q,

according to the analyses, we have sulphur low, while silicon gradually increases, and with this increase we find a result exactly like that noticed in my own experiments. These results therefore confirm my previous conclusion that a suitable proportion of silicon exerts a beneficial influence on the properties of cast iron.

XVI.—*On a Method of Separation and Estimation of Zirconium.*

By G. H. Bailey, D.Sc., Ph.D., Assistant Lecturer on Chemistry at the Owens College.

The Preparation of a New Oxide, Zr_2O_5.

Last winter, whilst making an analysis of the mineral koppite, in Professor Bunsen's laboratory in Heidelberg University, it was found that one of the precipitates, containing ferric oxide, yielded a notable quantity of zirconia on treatment with tartaric acid and ammonium sulphide. Thinking it might consist, at least in part, of titanic acid, this precipitate was redissolved and hydrogen peroxide was added to the acid solution; no trace of the reddish-brown coloration characteristic of titanic acid was observed, but a white bulky precipitate was formed. This was well washed, and heated gently with the addition of hydrochloric acid and potassium iodide; iodine was liberated, indicating that the substance was a higher oxidation product of zirconium. To confirm this, pure double fluoride of potassium and zirconium was taken, and having been converted into the sulphate was treated in the same manner with hydrogen peroxide; the precipitate obtained agreed in all respects with that already observed in the examination of the koppite.

About the same time, though I did not see it till months afterwards, a paper by Clève appeared on the action of hydrogen peroxide on the rare earths (*Bull. Soc. Chim.*, **43**, 53), showing that he had obtained a peroxide of zirconium having the composition ZrO_3. This he prepared by precipitating with ammonia a solution of the sulphate containing hydrogen peroxide, and washing the precipitate by decantation. Such a method is open to the objections that being precipitated partially by the hydrogen peroxide and partially by the ammonia, the product consists of a mixture of hydrate of zirconia and the higher oxide; that with such a substance as zirconia it is doubtful whether the whole of the excess of hydrogen peroxide can be washed out by decantation; and, lastly, that under the circumstances, as pointed out

by Clève himself, notable quantities of nitric acid are produced, no doubt arising from the reaction between the ammonia and the hydrogen peroxide. On reading his paper, therefore, in view of certain results which had been arrived at already, it appeared to me desirable to continue the work, and ascertain whether it was possible by the addition of hydrogen peroxide alone, to prepare an oxide of definite composition, and whether a complete separation of zirconium might not be effected by its means. A quantity of potassium zirconium fluoride was prepared from zircons by Wöhler's method. The melt was powdered, digested with water and filtered hot, the process being repeated as long as any of the salt entered into solution; the double fluoride crystallised out on cooling. The insoluble residue contained iron and strontium in tolerable quantity, whilst the zirconium salt was somewhat yellow from the presence of a small quantity of iron. At this stage, a separation of the iron was not considered necessary. The salt was treated with excess of concentrated sulphuric acid to expel the hydrofluoric acid, and the solution after dilution with water was precipitated directly with hydrogen peroxide. The precipitate thus obtained was quite free from iron, and after washing out any free hydrogen peroxide and potassium salts it was preserved in the moist state. Three months afterwards this compound was subjected to a quantitative examination.

A portion of the moist oxide was introduced into a small flask and distilled with hydrochloric acid, the product of the reaction being passed into a solution of potassium iodide in the manner adopted in iodine titrations. The amount of iodine liberated was estimated by Bunsen's method, using an approximately decinormal solution of iodine and weak sulphurous acid. At the conclusion of the experiment, after the contents of the flask had been well boiled, and no more iodine was set free, the zirconium was precipitated as hydrate by the addition of ammonia, independent determinations having shown that the zirconium undergoes complete precipitation in this way, and that none of it distills over into the solution of potassium iodide. The precipitate, washed and ignited, gave the amount of zirconia. In all cases this was snow-white, and showed no trace of iron. The following is one of several concordant observations made in this way:—

	Gram.	
Iodine set free, equivalent to 17·2 c.c. of standard solution	= 0·2494	
ZrO_2 found	= 0·2520	
Zr calculated from ZrO_2	= 0·18602	
O „ „	= 0·06598	=0·08181
O „ iodine liberated ..	= 0·01583	

From these numbers it appears that the peroxide is Zr_2O_5. The percentage composition is—

	Found.	Calculated.
Zr	69·455	69·284
O............	30·545	30·716

O = 15·96, Zr = 90.

Clève's results lead one to anticipate an oxide of a somewhat unstable and ill-defined character, and so it might have come about that after three months' keeping, the compound, though answering so well to the composition Zr_2O_5, had yet lost oxygen during this time. A fresh portion was therefore precipitated with hydrogen peroxide, and after being well washed and the water removed at the filter-pump, it was subjected to analysis in the same way as the previous specimen, the following results being obtained :—

		Gram.	
Iodine set free, equivalent to 6·9 c.c. of standard solution	=	0·10005	
ZrO_2 found	=	0·1032	
Zr calculated from ZrO_2	=	0·07618	
O „ „	=	0·02702	=0·03333
O „ iodine liberated....	=	0·00631	

The percentage composition is—

Zr	69·564
O	30·436

a result agreeing with the previous one, and indicating that the oxide is of a very definite and stable nature. The slight oxygen deficiency that does occur may be due to a retention occasioned by the unavoidable dilution of the hydrochloric acid used through the oxide being in the moist state. This is rendered the more probable, since with a more dilute acid the oxygen was 0·48 per cent. low, and using hydrochloric acid diluted with its own bulk of water, the deficiency was 0·85 per cent. The composition of the oxide obtained by precipitating a solution of zirconia in dilute sulphuric acid by means of hydrogen peroxide, is therefore Zr_2O_5. It is worthy of remark, that whereas zirconia when freshly precipitated dissolves in the minimum quantity of very dilute sulphuric acid, this higher oxide is much less readily acted on, and indeed by treatment with cold dilute acid, a separation of the two oxides may be made. In the formation of such an oxide, therefore, as in many of its salts, zirconium shows distinct proclivities towards the nitrogen group of elements, and more particularly towards niobium, tantalum, and vanadium.

Zr_2O_5 *as a means of Separating and Estimating Zirconium.*

The preparation of zirconia free from traces of other elements is a matter of considerable detail, and where iron, titanium, niobium, and some other of the rarer elements are present, it is only effected with difficulty. For the estimation of zirconium in minerals which contain but small quantities of this element, there is no process that can be considered satisfactory. At the same time, it is by no means improbable that zirconium is much more widely distributed in the mineral world than we have as yet direct evidence of. Hydrogen peroxide presents us with a means of separation. A very dilute solution of this reagent does not effect the precipitation of zirconium, but, with a moderately concentrated solution, the precipitation is complete. Clève has pointed out that iron and alumina are not precipitated by it. Titanium gives a coloration, and forms a higher oxide, but this remains in solution, and the pentoxide of zirconium precipitated from a solution containing titanium salts was found to be quite free from titanium. Niobium and tantalum also appear to give no precipitate with hydrogen peroxide, nor do tin, silica, or indeed any of those elements which usually occur along with zirconium, and are difficult to separate from it.

The examination of the reaction is not yet complete, the results however, obtained up to this time are summed up briefly in the following statements. Hydrogen peroxide of such a strength as to yield 120 vols. of oxygen on heating (Thénard's strongest peroxide gave 475 vols.) precipitated the Zr_2O_5 *immediately* and *completely* from a solution of zirconia in sulphuric acid, containing considerable excess of the acid. If its strength were such as to yield only 20 vols. of oxygen, the precipitation occurred after a few seconds, and was not quite complete; on standing some time, however, in a closed tube, it was found that even with this weaker solution every trace of zirconium had been precipitated.

By the use of hydrogen peroxide it is therefore possible—

(1.) To prepare most readily pure compounds of zirconium.

(2.) To separate even small quantities of this element in minerals.

(3.) To make a quantitative estimation of zirconium in a direct and rapid manner. I propose to continue the examination of the reaction, and hope somewhat later to give such further details as may be of interest.

XVII.—*Notes on an Analysis of Koppite.*

By G. H. Bailey, D.Sc., Ph.D., Assistant Lecturer on Chemistry at the Owens College.

Appended are the results of the analysis of a specimen of this mineral from the Kaiserstuhl referred to in the previous paper. The analysis made by Knop and Rammelsberg is given in the second column:—

		Knop and Rammelsberg.
Nb_2O_5	61·64	62·18
TiO_2	0·52	—
ThO_2	—	3·00
ZrO_2	3·39	—
Oxides of Ce, La, Di	6·89	6·69
FeO	3·01	1·80
CaO	16·61	16·00
MgO	1·62	0·40
Na	3·58	5·58
K	0·36	4·23
F	Not estimated	(6·23)

(1.) The whole of the work of solution and digestion was done in platinum vessels. Forty times its weight of concentrated sulphuric acid was used for dissolving the mineral, a clear solution being obtained when the latter was added in small successive portions to the boiling acid. For such analyses, sulphuric acid is to be recommended in preference to hydrogen potassium sulphate.

(2.) The titanic acid was estimated by Weller's colorimetric method (*Ber.*, **15**, 2592) with hydrogen peroxide.

(3.) Rammelsberg, in another analysis, gives the percentage of fluorine as 2·9, and this is probably more typical; at any rate the specimen examined by me contained very little fluorine indeed.

(4.) It is well known that substances such as niobic acid and zirconia readily pass through the pores of the filter-paper when filtering under pressure, and to avoid this it is usual to add to the solution ammonium acetate. The addition of this salt is some trouble, and increases the risk of introducing impurity in the course of the analysis. It was found possible to filter without its addition by using the following device:—A third tube or a T-tube was introduced into the filtering arrangement, and partially closed by the pressure of a screw clamp on thick pump tubing attached to the tube. Supposing such a valve

admits air at 200 mm. pressure, then the pressure at the pump cannot rise beyond this point. So long as the pressure at the pump continues to rise (as it does all the time in the ordinary process of filtering) the filtrate passes through milky; when it reaches the limit determined by the valve, it begins to go through clearer, and presently quite clear. The milky filtrate may now be poured back and the filtration proper commenced. No trouble will be experienced in getting a clear filtrate. If the valve, however, is closed somewhat and the pressure at the pump rises, the oxide is again forced through and the filtrate becomes milky. The same has been found to hold with barium sulphate. Most of the work embodied in these two papers was done under the direction of Professor Bunsen, and I am indebted to him for many valuable suggestions and for his ever ready advice.

XVIII.—*Benzoylacetic Acid and some of its Derivatives.* Part IV.

By W. H. Perkin (Jun.), Ph.D., and A. Calman, Ph.D.

In the three previous parts of this paper, the preparation and properties of ethylic benzoylacetate and a few of its derivatives were described, and the close resemblance between these and the ethylic acetoacetate derivatives pointed out. As, however, there were still several doubtful points which required clearing up, a further examination of the derivatives of benzoylacetic acid was undertaken. The results of this investigation we now lay before the Society. Before proceeding with this research, it was thought probable that if methylic benzoylacetate were substituted for the ethylic salt as the starting point, more crystalline products might be obtained; it being a well-known fact that methylic salts crystallise more easily as a rule than ethylic.

The mode of preparing methylic benzoylacetate is exactly analogous to that of the ethylic salt (Trans., 1884, 170), the only difference being that methylic phenylpropiolate* must be substituted for ethylic phenylpropiolate.

The crude methylic benzoylacetate produced by the action of sulphuric acid on methylic phenylpropiolate is a brownish oil which does not solidify at 0°. To purify it, it is shaken with fairly con-

* This is easily produced by treating phenylpropiolic acid with methyl alcohol and hydrogen chloride. It is a colourless oil.

centrated caustic potash solution and animal charcoal, and filtered, the temperature being kept as low as possible by adding ice. The filtrate, which should be perfectly clear and free from oily drops, is then mixed with ice and acidulated with dilute sulphuric acid; this causes the precipitation of an oil, which is separated from the acid liquid by agitation with pure ether. The ethereal solution, after being washed with dilute sodic carbonate, is dried over calcic chloride, filtered, and the ether distilled off; an almost colourless oil is left behind, which after standing for a week over sulphuric acid in a vacuum gave the following numbers on analysis :—

0·1800 gram substance gave 0·0913 gram H_2O and 0·4440 gram CO_2.

	Found.	Theory. $C_6H_5\cdot CO\cdot CH_2\cdot COOCH_3$.
C	67·27 per cent.	67·41
H	5·62 ,,	5·62
O	27·11 ,,	26·97

Methylic benzoylacetate appears to be more stable than the ethylic salt, it is certainly not so easily decomposed by distillation.

On the addition of ferric chloride to the alcoholic solution, it gives the same beautiful violet coloration as the ethereal salt. If methylic benzoylacetate is added to an ethereal solution of sodic ethylate, and the whole allowed to remain for a short time, a thick white precipitate separates which is the sodium-derivative. In order to purify it, it is collected as rapidly as possible, well washed with dry ether, and dried over sulphuric acid in a vacuum. The following numbers were obtained on analysis :—

0·3470 gram substance gave 0·1206 gram Na_2SO_4.

	Found.	Theory. $C_6H_5\cdot CO\cdot CHNa\cdot COOCH_3$.
Na	11·14 per cent.	11·50 per cent.

Prepared as above this sodium-derivative is a white amorphous powder easily soluble in water and hot alcohol.

It is extremely stable, much more so than the sodium-derivative of ethylic benzoylacetate, and behaves much like a salt of an acid. On acidifying its aqueous solution with dilute sulphuric acid, methylic benzoylacetate is reprecipitated together with a certain amount of benzoylacetic acid.

When treated with benzyl chloride in alcoholic solution, it gave a product, which after repeated fractioning boiled fairly constantly between 250° and 255° (50 mm. pressure). It gave the following numbers on analysis :—

0·214 gram substance gave 0·5955 gram CO_2 and 0·117 gram H_2O.

	Found.	Theory. $C_6H_5·CO·CH(C_7H_7)·COOCH_3$.
C	75·89 per cent.	75·00 per cent.
H	6·07 "	6·25 "
O	17·04 "	18·75 "

This compound, therefore, was probably methylic benzylbenzoylacetate. A few other derivatives of methylic benzoylacetate were also prepared, but as they did not crystallise, and as the yield was in every case inferior to that obtained when ethylic benzoylacetate was used, the remainder of this research was carried out with the ethylic salt.

Ethylic Methylbenzoylacetate.

To prepare this compound, 11 grams of sodium were dissolved in 120 grams of absolute alcohol, and a mixture of 90 grams of ethylic benzoylacetate and 80 grams of methylic iodide were slowly added, taking care to cool well during the operation. The clear solution was then heated at 100° for three hours in a soda-water bottle, when the reaction was complete. In order to isolate the product, water was added, and the liquid extracted twice or thrice with ether. The ethereal solution was then well washed with water, dried over potassic carbonate, and the ether distilled off; the dark-brownish coloured oil thus obtained was further purified by fractioning under a pressure of 300 mm.

By the first distillation, almost the whole went over between 230—240°, and after repeated refractioning a colourless oil of aromatic odour was obtained, boiling constantly at 235° (300 mm). It gave the following results on analysis:—

0·1227 gram substance gave 0·3135 gram CO_2 and 0·788 gram H_2O.

	Found.	Theory. $C_6H_5·CO·CH(CH_3)·COOC_2H_5$.
C	69·69 per cent.	69·90 per cent.
H	7·13 "	6·80 "
O	23·18 "	23·40 "

This compound is therefore ethylic methylbenzoylacetate. It boils at—

235° under a pressure of 300 mm.
226—227° under a pressure of 225 mm.

Its alcoholic solution gives no coloration with ferric chloride. If sodic ethylate is added to its ethereal solution, a thick white sodium-derivative is precipitated, which is decomposed on the addition of much water.

In order, if possible, to obtain the free methylbenzoylacetic acid, the pure ethereal salt was mixed with pure concentrated sulphuric acid, and allowed to stand at ordinary temperatures for three weeks. The product, which was slightly brownish, was then poured on ice, and the solution several times extracted with pure ether. On drying this ethereal solution over calcic chloride and evaporating, an almost colourless oil was left which did not crystallise, even after standing for several days over sulphuric acid in a vacuum, and therefore was not analysed. When treated with dilute ammonia, the greater part dissolved, leaving a small quantity of a brownish-coloured oil.

When heated in a test-tube, carbonic anhydride was given off, and the residue on fractioning went over almost entirely between 205° and 215° as a colourless oil, which was without doubt ethyl phenyl ketone, $C_6H_5 \cdot CO \cdot CH_2 \cdot CH_3$ (b. p. 210°).

The solution of the crude acid was coloured reddish-brown on the addition of a drop of ferric chloride. It is therefore almost certain that this oily acid consisted for the most part of methylbenzoyl-acetic acid, rendered impure by the presence of oily decomposition products which prevented it from crystallising.

Action of Phosphorous Pentachloride on Ethylic Methylbenzoylacetate. α-Methyl-β-chlorocinnamic Acid.

On treating ethylic benzoylacetate with pentachloride of phosphorus, it is transformed (Trans., 1885, 256) into a chlorocinnamic acid, $C_6H_5 : CH : CCl : COOH$, in which the chlorine-atom appears to be in the α-position. From the method of formation, however, β-chlorocinnamic acid should be formed according to the equation—

$$\text{I. } C_6H_5 \cdot CO \cdot CH_2 \cdot COOEt + 2PCl_5 = C_6H_5 \cdot CCl_2 \cdot CH_2 \cdot COCl + EtCl + 2POCl_3.$$

$$\text{II. } C_6H_5 \cdot CCl_2 \cdot CH_2 \cdot COCl + H_2O = C_6H_5 \cdot CCl : CH \cdot CO\,OH + 2HCl.$$

It appeared therefore interesting to follow up this reaction, and in the first place to examine the action of pentachloride of phosphorus on a substituted ethylic benzoylacetate.

For this purpose, 10 grams of ethylic methylbenzoylacetate were dissolved in 50 grams of phosphorous oxychloride, and then 25 grams of phosphorous pentachloride were slowly added, the whole being well cooled with ice during the operation. After standing for about an hour, the mixture was finally heated a short time on a water-bath and then poured on ice. When all the oxychloride had been decomposed, a yellowish oil was left, which was separated from the acid liquid by extraction with ether. The ethereal solution was shaken

with dilute sodic hydrate to remove any acids which had been formed, dried over calcic chloride and the ether distilled off.

In this way a yellowish oil was obtained which was further purified by fractioning under reduced pressure (300 mm.). Almost the whole of it went over in the first distillation between 225° and 240°, and after repeated fractioning an oil was obtained boiling constantly at 230—233° (300 mm.). This gave the following numbers on analysis :—

I. 0·1996 gram substance gave 0·4700 gram CO_2 and 0·1076 gram H_2O.

II. 0·1536 gram substance gave 0·0952 gram AgCl.

	Found.			Theory.	
	I.	II.		$C_6H_5 \cdot CCl : C(CH_3) \cdot COOC_2H_5$.	
C	64·22	—	per cent.	64·14	per cent.
H	5·99	—	,,	5·79	,,
Cl	—	15·34	,,	15·81	,,

This substance therefore is ethylic α-methyl-β-chlorocinnamate, formed according to the following equation :—

$$C_6H_5 \cdot CO \cdot CH(CH_3) \cdot COOC_2H_5 + PCl_5 = C_6H_5 \cdot CCl : C(CH_3) \cdot COOC_2H_5 + HCl + POCl_3.$$

On examining the alkaline solution obtained by extracting the crude product of the action of phosphorus pentachloride on ethylic methylbenzoylacetate, it was found that when this was acidified with dilute sulphuric acid, a quantity of an organic acid was precipitated in white flakes. These when collected, dried on a porous plate, and crystallised several times from boiling light petroleum, were obtained in the form of colourless needles, which gave the following results on analysis :—

I. 0·1890 gram substance gave 0·4213 gram CO_2 and 0·086 gram H_2O.

II. 0·2413 gram substance gave 0·1555 gram AgCl.

	Found.			Theory.	
	I.	II.		$C_6H_5 \cdot CCl : C(CH_3) \cdot COOH$.	
C	61·07	—	per cent.	60·79	per cent.
H	4·58	—	,,	5·06	,,
Cl	—	18·07	,,	17·95	,,

This acid is therefore α-methyl-β-chlorocinnamic acid. It melts at 116°, and can be distilled in small quantities almost without decomposition. It dissolves easily in alcohol, ether, chloroform, benzene, and acetic acid, more sparingly in cold light petroleum. When

treated with concentrated nitric acid, crystalline nitro-derivatives are formed, which, however, were not further examined.

The silver salt of this acid was prepared by adding silver nitrate to a neutral solution of the ammonic salt. After collecting and washing with water, it was obtained as a white mass, which when dried over sulphuric acid in a vacuum gave the following numbers on analysis :—

0·3175 gram substance gave 0·1482 gram AgCl.

	Found.	Theory. $C_6H_5\cdot CCl:C(CH_3)\cdot COOAg$.
Ag......	35·20 per cent.	35·64 per cent.

On heating this salt, it is decomposed, a colourless oil being given off which is probably chloromethylstyrene. In this chloromethylcinnamic acid, it is obvious that the chlorine-atom must be in the β-position, the α-position being occupied by the methyl-group.

α-Methyl-β-phenylhydroxypropionic Acid.

Ethylic benzoylacetate is easily reduced when treated with sodium amalgam, β-phenyllactic acid being formed (Trans., 1885, 253), thus—

$$C_6H_5\cdot CO\cdot CH_2.COOC_2H_5 + H_2 + H_2O = C_6H_5\cdot CH(OH)\cdot CH_2\cdot COOH + C_2H_5\cdot OH.$$

In order to determine whether this reaction is a general one, it was determined to try the action of reducing agents on a substituted ethylic benzoylacetate. For this purpose, pure ethylic methylbenzoylacetate was dissolved in dilute alcohol, and sodium amalgam slowly added, the whole being cooled from time to time with cold water. After 24 hours, the alkaline liquid was separated from the mercury, evaporated on a water-bath until all the alcohol had been driven off, acidified with dilute sulphuric acid, and extracted six times with ether. On drying over calcic chloride and distilling off the ether, a thick oil was left, which did not crystallise even after remaining for some hours over sulphuric acid in a vacuum. In order to purify this substance, it was dissolved in a slight excess of baryta-water, the excess of baryta precipitated by carbonic anhydride and the whole filtered. The filtrate was then acidified with dilute hydrochloric acid and again extracted with ether. On distilling off the ether, a colourless oil remained, which solidified on standing. The crystalline mass was first spread out on a porous plate to remove traces of oily matter, and then dissolved in a little boiling benzene. On cooling, the acid crystallised out in colourless needles which gave the following numbers on analysis :—

I. 0·1920 gram substance gave 0·4695 gram CO_2 and 0·1175 gram H_2O.

II. 0·2671 gram substance gave 0·6488 gram CO_2 and 0·1666 gram H_2O.

	Found. I.	Found. II.	Theory. $C_6H_5 \cdot CH(OH) \cdot CH(CH_3) \cdot COOH$.
C	66·35	66·24 per cent.	66·67 per cent.
H	6·80	6·93 "	6·67 "
O	26·85	26·83 "	26·67 "

α-Methyl-β-phenylhydroxypropionic acid when quite pure melts at 124—125°. It is very easily soluble in alcohol, ether, acetone, and hot water, sparingly soluble in chloroform, bisulphide of carbon, and light petroleum. It crystallises beautifully from boiling water in nodular masses, and from a solution of equal parts of light petroleum and benzene in flat needles. If the free acid is heated in a test-tube, water is given off and an oil distils over, which on cooling for the most part solidifies, and smells strongly of benzaldehyde.

When mixed with concentrated sulphuric acid, it becomes yellowish, and on warming it dissolves forming a reddish-brown solution.

The *ammonium* salt of α-methyl-β-phenylhydroxypropionic acid crystallises from water in beautiful feathery needles. The *silver* salt is easily obtained on adding silver nitrate to a neutral solution of the ammonium salt as a heavy white crystalline precipitate, which gave the following numbers on analysis:—

0·2773 gram substance gave 0·1036 gram silver.

	Found.	Theory. $C_6H_5 \cdot CH(OH) \cdot CH(CH_3) \cdot COOAg$.
Ag......	37·36 per cent.	37·63 per cent.

This silver salt, when heated, was rapidly decomposed into silver, and a colourless oil, which smelt strongly of benzaldehyde.

Ethylic Propylbenzoylacetate.

This ethereal salt was prepared by heating a mixture of ethylic benzoylacetate (50 grams) with sodic ethylate (Na = 6 grams) and an excess of propylic iodide (50 grams) for four hours at 100° in a soda-water bottle.

The product was isolated in the same way as the ethylic methylbenzoylacetate and purified by fractioning under diminished pressure (300 mm.). In the first distillation, almost all went over between 240° and 260°, and after repeated refractioning the ethylic propyl-

benzoylacetate was obtained pure as a colourless oil, boiling constantly between 250° and 252° (300 mm.). On combustion it gave the following numbers :—

0·3358 gram substance gave 0·8886 gram CO_2 and 0·2423 gram H_2O.

	Found.	Theory. $C_6H_5{\cdot}CO{\cdot}CH(C_3H_7){\cdot}COOC_2H_5$.
C	72·15 per cent.	71·79 per cent.
H	8·01 ,,	7·69 ,,
O	20·52 ,,	20·52 ,,

Ethylic propylbenzoylacetate is a colourless oil of aromatic odour, which does not solidify at 0°. It is slightly soluble in caustic potash. When treated with sodic ethylate, it gives a sodium-derivative. Its alcoholic solution gives no coloration with ferric chloride.

When quite pure, it was found to have the following boiling points :—

250—252° (300 mm.)
238—239 (225 ,,)

Butyl Phenyl Ketone.

In order to obtain this ketone, ethylic propylbenzoylacetate was heated in a flask connected with a reflux condenser with dilute alcoholic potash for six hours, at the end of which time decomposition was complete. On adding water, an oil was precipitated, which was separated from the alkaline solution by extraction with ether. The ethereal solution, after being well washed with water, was dried over potassic carbonate, and the ether distilled off.

In this way a dark-brownish oil was obtained, which after repeated fractioning boiled constantly between 236° and 238° (720 mm.), and on analysis gave numbers, showing it to be butyl phenyl ketone :—

I. 0·1158 gram substance gave 0·3441 gram CO_2 and 0·0957 gram H_2O.

II. 0·1805 gram substance gave 0·5373 gram CO_2 and 0·1528 gram H_2O.

	Found.		Theory.
	I.	II.	$C_6H_5{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$.
C	81·05	81·19 per cent.	81·48 per cent.
H	9·19	9·28 ,,	8·64 ,,
O	9·75	9·53 ,,	9·88 ,,

This ketone is formed from ethylic propylbenzoylacetate by hydrolysis and splitting off of carbonic anhydride according to the following equation :—

$$C_6H_5\cdot CO\cdot CH(C_3H_7)\cdot COOC_2H_5 + 2KOH = C_6H_5\cdot CO\cdot CH_2\cdot C_3H_7 + K_2CO_3 + C_2H_5\cdot OH.$$

It is a colourless oil of agreeable aromatic odour, and boils at 236—238° (720 mm.) without decomposition.

Action of Phosphorus Pentachloride on Ethylic Propylbenzoylacetate.

It was next thought interesting to try the action of phosphorus pentachloride on ethylic propylbenzoylacetate. 10 grams of the substance were dissolved in 35 grams of oxychloride of phosphorus, 18 grams of phosphorus pentachloride were slowly added, and the whole allowed to remain until the principal reaction was over. The mass was then heated on a water-bath for half an hour, poured into ice, and from time to time stirred round until the oxychloride of phosphorus was completely decomposed. After extracting with ether, the ethereal solution was treated with dilute sodic hydrate, then dried over calcic chloride and the ether distilled off. In this way, a heavy yellow oil was obtained which after repeated fractioning in a vacuum was obtained pure as a colourless oil boiling between 247° and 249° (300 mm.).

On analysis the following numbers were obtained:—

I. 0·2251 gram substance gave 0·5480 gram CO_2 and 0·1438 gram H_2O.

II. 0·2085 gram substance gave 0·5075 gram CO_2 and 0·1228 gram H_2O.

III. 0·1330 gram substance gave 0·0755 gram AgCl.

	Found.				Theory.
	I.	II.	III.		$C_6H_5\cdot CCl:C(C_3H_7)\cdot COOC_2H_5$.
C	66·42	66·45	—	per cent.	66·67 per cent.
H	7·09	6·56	—	,,	6·75 ,,
Cl	—	—	14·07	,,	13·89 ,,

This substance was therefore ethylic α-propyl-β-chlorocinnamate, formed according to the equation—

$$C_6H_5\cdot CO\cdot CH(C_3H_7)\cdot COOC_2H + PCl_5 = C_6H_5\cdot CCl:C(C_3H_7)\cdot COOC_2H_5 + POCl_3 + HCl.$$

The alkaline solution, formed by treating the ethereal solution of the crude product of the action of phosphorus pentachloride on ethylic propylbenzoylacetate with sodic hydrate was next examined. On acidifying with dilute sulphuric acid, yellow flakes were precipitated, which were collected and well washed with water. They were

then dried on a porous plate and purified by several recrystallisations from light petroleum.

The following analytical results showed that the compound is α-propylβ-chlorocinnamic acid :—

I. 0·2030 gram substance gave 0·4738 gram CO_2 and 0·1022 gram H_2O.

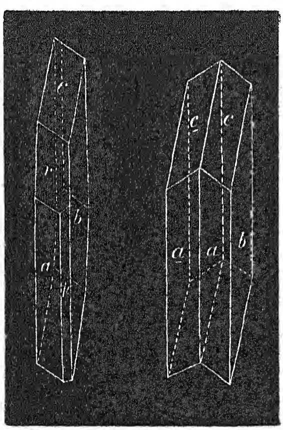
II. 0·2246 gram substance gave 0·5289 gram CO_2 and 0·1156 gram H_2O.

III. 0·2839 gram substance gave 0·1789 gram AgCl.

	Found. I.	II.	III.		Theory. $C_6H_5 \cdot CCl : C(C_3H_7) \cdot COOH$.
C	63·66	64·23	—	per cent.	64·29 per cent.
H	5·62	5·72	—	"	5·80 "
Cl	—	—	15·39	"	15·63 "

α-Propyl-β-chlorocinnamic acid melts at 121°, and sublimes in long colourless needles when carefully heated. It is easily soluble in alcohol, ether, chloroform, benzene, and acetic acid, more sparingly in cold light petroleum. By slowly cooling its solution in boiling light petroleum, it is obtained in beautiful prisms, which Professor Haushofer was kind enough to measure. He gave us the following description :—

Crystalline System. Triclinic.



$a : b : c := 0·7967 : 1 : 0·7403$

$\alpha = 122° \; 33'$

$\beta = 106 \;\; 21$

$\gamma = \;\; 69 \;\; 25$

$\infty\breve{P}\infty \; (0\bar{1}0) = b$

$\infty\bar{P}\infty \; (100) = a$

$0P \; (001) = c$

$\infty P'_{|} \; (110) = p$

$'\bar{P}'\infty \; (101) = r$

It forms tabular shaped twinned crystals on the surface b, with which the two surfaces a form a projecting angle in front, and a re-entering angle behind of 151° 22′ (measurement 151° 22—42′). The surfaces c form a projecting angle above and below a re-entering

angle of 121° 19′. The re-entering angle between the surfaces c could not be measured, as the crystals were irregular at the ends.

The surfaces b are generally curved, and not adapted for measurement, the edges in most of the crystals are broken up, but occasionally they are fully developed, and brilliant as the diamond. No single crystals were noticed.

The surfaces p are usually wanting in the twins, often r also.

	Measured.		Calculated.	
$a : b$ =	*75°	41′	—	—
$a : c$ =	*96	44	—	—
$b : c$ =	*119	16	—	—
$a : r$ =	*133	52	—	—
$b : p$ =	*140	39	—	—
$r : b$ =	101	43	101°	56′
$c : c$ =	121	19	121	19 (in the twins).

In convergent polarised light two systems of rings are observed on the surface b of the twins, the optical axes of which belong to both the twins.

The silver salt of the acid, prepared by precipitating a neutral solution of the ammonium salt with silver nitrate, is a thick white amorphous mass, almost insoluble in water. The analysis gave the following numbers:—

0·4945 gram substance gave 0·2165 gram AgCl.

	Found.	Theory. $C_6H_5·CCl : C(C_3H_7)·COOAg$.
Ag......	32·95 per cent.	32·25 per cent.

Ethylic Isopropylbenzoylacetate.

In order to obtain this substance, 50 grams of ethylic benzoylacetate were heated with 6 grams of sodium and an excess of isopropylic iodide for six hours at 100°. Water was then added, and the product isolated in the usual manner. On distilling the crude substance, almost all went over at 225—245° (225 mm.), and on repeated refractioning an oil was obtained boiling constantly at 236—237° (225 mm.), which gave the following numbers on analysis:—

0·2760 gram substance gave 0·7230 gram CO_2 and 0·188 gram H_2O.

	Found.	Theory. $C_6H_5·CO·CH[C(CH_3)_2]·COOC_2H_5$.
C......	71·45 per cent.	71·79 per cent.
H......	7·61 ,,	7·70 ,,
O......	20·94 ,,	20·51 ,,

Ethylic isopropylbenzoylacetate is an agreeably smelling oil. Its boiling point is about 2° lower than that of the normal propylic derivative previously described.

Isobutyl Phenyl Ketone.

This ketone was prepared by digesting ethylic isopropylbenzoylacetate with dilute alcoholic potash for about six hours. The brownish-coloured product was then diluted with water and several times extracted with ether. After distilling off the ether, a dark-coloured oil was left, which was easily obtained colourless by distillation. On repeatedly refractioning it, it boiled constantly at 227—228° (720 mm.), and gave on analysis the following numbers agreeing with the formula $C_6H_5 \cdot CO \cdot CH_2 \cdot CH(CH_3)_2$:—

0·1605 gram substance gave 0·4775 gram CO_2 and 0·1315 gram H_2O.

	Found.	Theory. $C_{11}H_{14}O$.
C	81·14 per cent.	81·48 per cent.
H	9·10 ,,	8·64 ,,
O	9·76 ,,	9·87 ,,

Isobutyl phenyl ketone is a colourless oil, of an agreeable aromatic odour.

This ketone has already been prepared by Popow (*Annalen*, **162**, 153) by distilling a mixture of benzoate and valerate of calcium. Popow gives the boiling point as 225—226°.

Isobutyl phenyl ketone does not combine with hydrogen sodium sulphite. On oxidation with chromic acid, benzoic, isobutyric, and acetic acids are formed (Popow).

Ethylic Isobutylbenzoylacetate.

This substance was prepared in exactly the same way as the isopropyl-derivative by heating ethylic benzoylacetate (1 mol.) with sodic ethylate (1 mol.) and an excess of isobutylic iodide at 100° for six hours. On fractioning the product, almost the whole of it went over between 230° and 260° (225 mm.) in the first distillation. Pure ethylic isobutylbenzoylacetate boils at 246—247° (225 mm.).

The following results were obtained on analysis :—

0·2257 gram substance gave 0·5960 gram CO_2 and 0·1620 gram H_2O.

	Found.	Theory. $C_6H_5 \cdot CO \cdot CH[CH_2 \cdot CH(CH_3)_2] \cdot COOC_2H_5$.
C	72·01 per cent.	72·58 per cent.
H	7·97 ,,	8·06 ,,
O	20·02 ,,	19·35 ,,

This ethereal salt has much the same properties as the isopropyl-derivative. The boiling point is about 10° higher.

Isoamyl Phenyl Ketone.

Ethylic isobutylbenzoylacetate is easily split up on heating it with dilute alcoholic potash into alcohol, carbonic anhydride, and isoamyl phenyl ketone, thus:—

$$C_6H_5{\cdot}CO{\cdot}CH[CH_2{\cdot}CH(CH_3)_2]{\cdot}COOC_2H_5 + 2KOH$$
$$= C_6H_5{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}[CH(CH_3)_2] + K_2CO_3 + C_2H_5{\cdot}OH.$$

The product of this reaction was isolated in the usual manner, and purified by fractioning. Isoamyl phenyl ketone is an aromatic smelling oil, boiling at 240—241° (720 mm.). Analysis:—

0·1870 gram substance gave 0·561 gram CO_2 and 0·156 gram H_2O.

	Found.	Theory. $C_6H_5{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH(CH_3)_2$.
C	81·82 per cent.	81·82 per cent.
H	9·27 "	9·09 "
O	8·91 "	9·09 "

In Part III of this research (Trans., 1885, 265—266) an acid, $C_{18}H_{12}O_5$, was described, which was obtained in small quantity from ethylic dibenzoylsuccinate by prolonged boiling with dilute sulphuric acid, and which from its method of formation was thought to be similarly constituted to carbopyrotritartaric acid.

This appeared the more probable from a small experiment which was tried at the time (*loc. cit.*, p. 271) on the action of concentrated sulphuric sulphuric acid on ethylic dibenzoylsuccinate; a compound was produced which on hydrolysis yielded the acid $C_{18}H_{12}O_5$ quantitatively, and was therefore probably its ethereal salt. In order to determine the nature of this decomposition, the experiment has since been carried out on a larger scale, in the following way:—

Finely-powdered ethylic dibenzoylsuccinate was shaken with about 10 times its weight of pure concentrated sulphuric acid, in which it soon dissolved, forming a colourless solution. This was allowed to remain for 12 hours, and then poured on to ice, when a thick almost colourless oil was precipitated, and was separated from the acid liquid by extracting it with ether. The ethereal solution was then well washed with water, and dried over calcic chloride. On distilling off the ether, an almost colourless oil remained, which instantly became solid on being touched with a glass rod. The mass was then dissolved in hot alcohol, from which it crystallised on cooling in beautiful canary-yellow prisms.

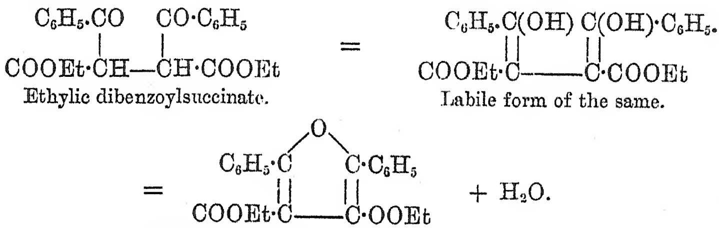
The analysis gave the following numbers:—

I. 0·1698 gram substance gave 0·4505 gram CO_2 and 0·0900 gram H_2O.

II. 0·2250 gram substance gave 0·5974 gram CO_2 and 0·1134 gram H_2O.

	Found. I.	Found. II.		Theory. $C_{12}H_{20}O_5$.	
C	72·36	72·41	per cent.	72·53	per cent.
H	5·89	5·60	"	5·89	"
O	21·75	21·99	"	21·98	"

This substance contains 1 mol. H_2O less than ethylic benzoylsuccinate, and appears to be formed according to the following equations :—



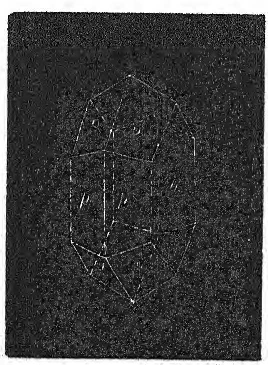
Ethylic dibenzoylsuccinate. Labile form of the same.

Ethylic diphenylfurfurandicarboxylate (1, 4, 2, 3).

Ethylic diphenylfurfurandicarboxylate [1, 4, 2, 3] melts at 86°, and is characterised particularly by the readiness with which it crystallises. It is easily soluble in chloroform, benzene, ether, alcohol, and light petroleum, and can be obtained in beautiful almost colourless prisms, by allowing the ethereal solution to evaporate slowly. Prof. Haushofer was kind enough to measure these. He gave me the following description of these crystals :—

Crystalline System. Rhombic.

$a : b : c = 0·9005 : 1 : 0·6309$



Pale sulphur-yellow transparent crystals of the combinations $P(111) = o$, $\infty\breve{P}\frac{1}{2}(210) = p$, $\infty\breve{P}\infty(010) = b$. Short prismatic in the vertical axis, usually tabular through development of the surfaces b.

	Measured.	Calculated.	
$o : o = (111)\ (11\bar{1}) =$	*86° 38′	— —	(Basal angle).
$o : o = (111)\ (1\bar{1}1) =$	*118 42	— —	(Macrodiagonal. Polar angle).
$o : o = (111)\ (1\bar{1}1) =$	125 10	125° 20′	(Brachydiagonal. Polar angle).
$p : p' = (210)\ (2\bar{1}0) =$	131 32	131 35	
$o : p = (111)\ (210) =$	130 37	130 47	
$o : p' = (111)\ (2\bar{1}0) =$	106 3	106 50	

The base of the plane the optical axis. In convergent polarised light the interference image of an axis (excentric in the direction of the angle pb) appears on the surface p.

When heated in small quantities, this ethereal salt distils almost without decomposition. Although the solution in chloroform does not decolorise bromine at ordinary temperatures, it does so easily on warming, hydrobromic acid being liberated. When treated with nitric acid, beautifully crystalline nitro-derivatives are formed. Ethylic diphenylfurfurandicarboxylate is not acted on by phosphorus pentachloride at ordinary temperatures. It dissolves in concentrated sulphuric acid, forming a colourless solution, which on heating becomes first brownish and then of a beautiful violet colour.

Diphenylfurfurandicarboxylic Acid [1, 4, 2, 3].

When ethylic dibenzoylsuccinate is boiled with dilute sulphuric acid, a small quantity of an acid is formed, which from previous analysis (Trans., 1885, 267) was found to have the formula $C_{18}H_{12}O_5$.

Owing to the small yield obtained by this reaction, it was only superficially examined. The same acid can, however, be obtained quantitatively by the hydrolysis of ethylic diphenylfurfurandicarboxylate with alcoholic potash. It is only necessary to digest the ethereal salt 15 minutes with an excess of alcoholic potash, to completely saponify it. At the end of the reaction, water is added, and the whole evaporated until all the alcohol has been driven off. On acidifying with dilute sulphuric acid, the acid is thrown down in white flakes. After collecting and recrystallising it from acetic acid (70 per cent.), it is easily obtained pure in colourless needles, melting at 238°.

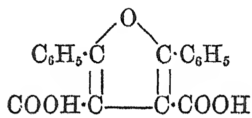
The following analyses confirm the formula previously assigned to this acid.

I. 0·1762 gram substance gave 0·4523 gram CO_2 and 0·0637 gram H_2O.

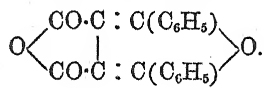
II. 0·1848 gram substance gave 0·4735 gram CO_2 and 0·0726 gram H_2O.

	Found.		Theory.
	I.	II.	$C_{18}H_{12}O_5$.
C	70·01	69·89 per cent.	70·13 per cent.
H	4·01	4·36 „	3·89 „
O	25·98	25·75 „	25·97 „

This compound is therefore diphenylfurfurandicarboxylic acid,



It melts at 238° to a colourless liquid, which when strongly heated splits up into the compound $C_{18}H_{10}O_4$ and water. This was described in Part III of this research (Trans., 1885, 268), and appears to be the anhydride of diphenylfurfurandicarboxylic acid,*



According to this interpretation, the re-formation of the acid $C_{18}H_{12}O_5$ by treating this body $C_{18}H_{10}O_4$ with alcoholic potash can be easily understood.

The salts of diphenylfurfurandicarboxylic acid were described in Part III of this research (Trans., 1885, 268), and the analyses of the silver and calcium salts given. Owing to the small quantity of acid which could be prepared at that time, no satisfactory results were obtained by the analysis of these salts. The experiments were therefore repeated with larger quantities of material. The *silver* salt was prepared by fractional precipitation of the ammonium salt with silver nitrate, and analysed with the following results :—

I. 0·2235 gram substance gave 0·3380 gram CO_2, 0·0520 gram H_2O, and 0·0925 gram Ag.

II. 0·2010 gram substance gave 0·3060 gram CO_2, 0·040 gram H_2O, and 0·0833 gram Ag.

III. 0·2750 gram substance gave 0·1130 gram Ag.

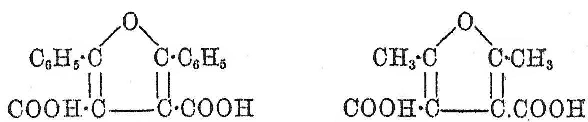
* This is also the opinion of Knorr (*Ber.*, 17, 2869).

	Found.				Old analyses.		
	I.	II.	III.		I.	II.	
C	41·25	41·51	—	p. c.	40·66	—	p. c.
H	2·59	2·21	—	„	2·32	—	„
Ag ...	41·39	41·44	41·09	„	40·52	40 25	„
O	14·77	14·84	—	„	16·50	—	„

Theory.	$C_{18}H_{10}O_5Ag_2$.
C..........	41·44 per cent.
H..........	1·91 „
Ag........	41·29 „
O..........	15·35 „

Diphenylfurfurandicarboxylic acid is therefore a simple bibasic acid forming salts of the formula $C_{18}H_{10}O_5M_2$.

From the method of formation of this acid it would at first sight appear probable that its constitution was exactly similar to that of carbopyrotritartaric acid, which Knorr has shown to be produced by the action of concentrated sulphuric acid on ethylic diacetylsuccinate:



Diphenylfurfurandicarboxylic acid. Dimethylfurfurandicarboxylic acid (carbopyrotritartaric acid).

There is, however, one great difference between these acids; carbopyrotartaric acid is easily decomposed on heating above its melting point into pyrotritartaric acid and carbonic anhydride,

$$C_8H_8O_5 - CO_2 = C_7H_8O_3,$$

whereas diphenylfurfurandicarboxylic acid is simply converted into its anhydride, as described above, the monocarboxylic acid corresponding with pyrotritartaric acid not having as yet been obtained.

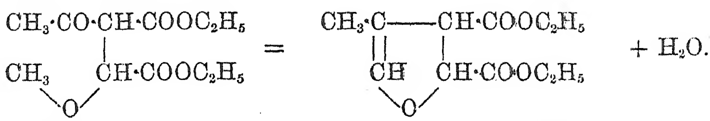
Lately Fittig (*Ber.*, **18**, 3410) has made it doubtful whether carbopyrotritartaric and pyrotritartaric acids really are furfurane-derivatives.

In his researches on the condensation of ethylic acetoacetate with succinic acid, he obtained an acid isomeric with carbopyrotritartaric acid, according to the equation—

$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}COOC_2H_5 + COOH{\cdot}CH_2{\cdot}CH_2{\cdot}COOH = \underset{\text{Methronic acid.}}{C_8H_8O_5} + H_2O + C_2H_5{\cdot}OH.$$

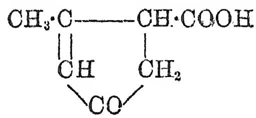
which at a temperature of 200—240° is converted quantitatively into pyrotritartaric acid and carbonic anhydride.

In this way, it is difficult to conceive how pyrotritartaric acid can contain two methyl groups, and Fittig therefore supposes that in the formation of ethylic carbopyrotritartrate from ethylic diacetylsuccinate condensation takes place in a way analogous to the formation of mesityl oxide from acetone.



Ethylic diacetylsuccinate. Ethylic carbopyrotritartrate.

Pyrotritartaric acid would then have the constitution—



It is therefore probable that the acids obtained from ethylic diacetylsuccinate and dibenzoylsuccinate by the same reaction, *i.e.*, by the action of dehydrating agents, are of an entirely different structure, the former being derivatives of pentamethylene, the latter of furfurane. From the experiments described above, it is scarcely possible that the acid $C_{18}H_{12}O_5$ can be a lactonic acid, as Fittig believes (*Ber.*, **18**, 3411).

In conclusion, we append for convenience sake tables of the boiling points of the homologues of ethylic benzoylacetate obtained in the course of this research, and of the homologues of acetophenone prepared by the hydrolysis of these ethereal salts.

Boiling points of the Ethylic Salts of Benzoylacetic Acid and its Homologues under 225 *mm. pressure.*

Ethylic benzoylacetate	220—225°
,, methyl benzoylacetate	226—227
,, ethyl benzoylacetate	231—232
,, propyl benzoylacetate	238—239
,, isopropyl benzoylacetate	236—237
,, allyl benzoylacetate	240—241
,, isobutyl benzoylacetate	246—247
Methylic benzylbenzoylacetate	250—255 (?) (50 mm. pressure).

	Boiling point under 720 mm. pressure.
Acetophenone..............	200°
Ethyl phenyl ketone	210
Propyl phenyl ketone	220—222
Allylacetophenone..........	235—238
Butyl phenyl ketone	236—238
Isobutyl phenyl ketone......	227—228
Diethylacetophenone........	229—231
Isoamyl phenyl ketone	240—241

Further experiments on ethylic benzoylacetate, and more especially on the behaviour of ethylic dibenzoylsuccinate with different reagents, are in progress.

XIX.—*The Chemical Action of Pure Cultivations of Bacterium Aceti.*

By A. J. BROWN.

THE following paper contains an account of experiments made for the purpose of investigating some of the chemical actions of a pure cultivation of *Bacterium aceti.*

Pasteur, in his "Mémoire sur la Fermentation Acétique," published in 1864, was the first to show that acetic fermentation is caused by a living micro-organism, which he named *Mycoderma aceti.* He further shows that the acetic acid formed during the fermentation is produced by the oxidation of ethylic alcohol by the oxygen in the air, this action being brought about by the ferment. Moreover, when the fermentation is weakened in certain ways, aldehyde is present, and if the fermentation is allowed to go on after the whole of the alcohol is oxidised, the acetic acid already formed becomes further oxidised to CO_2 and H_2O. Pasteur also believes that succinic acid in small quantity is always formed as a bye-product during the acetic fermentation.

E. Wurm (*Dingl. polyt. J.*, **235**, 225) investigated the acetic fermentation, and confirms Pasteur's statement that the formation of vinegar from alcoholic liquids is due to an organised ferment.

In the *Comptes rendus* of July, 1880, p. 236, Boutroux describes an action of the acetic ferment on glucose, but this paper will be more fully referred to later on.

Cohn (*Biol. d. Pflanzen*, **2**, 173), and more particularly Hansen (*Meddelser fra Carlsberg-Laboratoriet*), have investigated the acetic ferment (*B. aceti*) morphologically, but do not appear to have studied its chemical action.

Before describing my experiments, I think it advisable in a research of this nature to describe the method of working, and the means used for the purification of the ferment.

As *B. aceti* is strictly an aërobic ferment, and consequently as my experiments required free access of air, the method of working with flasks or test-tubes plugged with sterilised cotton-wool was found very suitable. All the vessels and cotton-wool used, and also the various liquids in which the ferment was grown, were sterilised with all the precautions advised by Klein ("Micro-organisms and Disease," *Practitioner*, 1884). No solution was considered sterilised and fit for use unless it had kept quite free from all forms of living organisms for at least a week at a temperature of 28°. Inoculation from one vessel to another was effected by means of a capillary glass tube freshly drawn out and pointed at one end, so that it could be forced through the cotton-wool plugs in the necks of the vessels, and each tube was not used more than once. The cotton-wool plugs of the vessels were kept covered with sterilised paper, and, before inoculating from one vessel to another, the surface of the plug was singed by a gas flame.

I found the most suitable method for obtaining a pure culture of *B. aceti* was a combination of Kleb's "Fractional" and v. Nägeli's "Dilution" methods. Inoculation in gelatin media did not give such satisfactory results, because *B. aceti* being so strictly aërobic it only grows on the immediate surface of the gelatin, and in such an attenuated film that it is difficult to detect it in its early stage of growth before it has spread over a considerable surface.

The *B. aceti* used in my experiments was originally taken from the surface of a beer that had been kept exposed to the air in a warm place until the acetic fermentation developed. This ferment was inoculated into the first of a series of 10 test-tubes, containing a sterilised solution of 2 per cent. ethylic alcohol in yeast water;* the inoculations being made from one tube to another as soon as a visible growth was observed (generally from 36 to 48 hours). Finally, the culture was further tested by the "dilution" method, and showed its purity by always producing a growth of *B. aceti* (or no growth at all) in the tubes into which the diluted ferment was inoculated. Further, if the reactions of this ferment, which I describe further on, are considered, the comparative simplicity of the action in some cases,

* Used by Pasteur, and prepared by boiling 7 per cent. yeast, pressed as dry as possible, in water, and filtering until quite bright.

and the want of action altogether in others, will leave no doubt that my experiments were made with a pure cultivation of acetic ferment. *B. aceti* has so many different forms of growth, that I do not consider the microscope alone gives much trustworthy aid in detecting foreign ferments mixed with it.

The mode of growth of pure *B. aceti* in alcoholic or sugar solutions, is in the form of a rather greasy pellicle covering the surface of the liquid, and inclined in its young stage of growth to creep up the moist sides of the containing vessel.

This pellicle varies in thickness from an almost invisible film on the surface of such a mixture as dextrose and Pasteur's solution, to the thickness of stout paper on diluted claret. Slight agitation easily breaks the surface of this pellicle, and, after its somewhat greasy surface is wet, it sinks to the bottom of the liquid, only, however, for another growth to form again on the surface, if the liquid still contains the proper nourishment for it. The liquid below the pellicle is usually turbid with isolated cells of the ferment, and, after a cultivation has been allowed to remain undisturbed for some weeks, a considerable deposit of the growth is found at the bottom. *B. aceti* is, strictly speaking, an aërobic ferment; if inoculated into solutions kept free from oxygen, it will not increase or produce any chemical changes in the liquid, but, nevertheless, is capable of living under these circumstances for a long time. I have kept an inoculated solution out of contact with air for six months without its showing any signs of growth, but on admitting filtered air a strong growth started in a few days.

Hitherto, two species of bacteria said to have the power of oxidising alcohol to acetic acid have been described, viz., the ordinary *B. aceti* with which we are now concerned, and the *B. Pasteurianum* of Hansen. There is, however, at least one other distinct species, about which I hope to say something in another communication. Under these circumstances it seems advisable to describe shortly the morphology of the species with which I have worked (viz., *B. aceti*).

B. aceti in its normal state, freshly growing as a pellicle on the surface of a liquid, appears under the microscope as a mass of cells about 2μ* in length, and slightly contracted in the middle, giving them a sort of figure of 8 appearance. These cells are united into chains of variable length, which are easily broken up by pressure of the cover-glass. Frequently the cells are quite divided in the middle, thus producing strings of micrococcus-like forms; both forms being sometimes found in the same chain. The above two forms are those

* No exact measurements of *B. aceti* can be given, as all the forms differ very much amongst themselves in size, varying with the different culture fluids, amount of acid, &c.

usually present when the ferment is growing vigorously at the surface of a liquid. But in the liquid below the surface film, and on the bottom of the containing vessel, abnormal forms are often found differing very much from the ordinary surface growth; this is more especially the case in old cultivations. These forms often attain the length of 10—15μ, or even more; in some cases their form is that of leptothrix threads of even thickness throughout their length; in others, the long cells are swollen out in two or three places along their length, giving them a most irregular appearance. These cells are generally of a dark-grey colour. At their ends a short chain of short rods or micrococci is sometimes observed. The other forms most frequently seen are short rods about 3μ in length, and micrococci about 1μ in diameter, floating freely in the culture liquid. My observations on the morphology of *B. aceti* agree very well with the drawings given by Hansen (*Meddelser fra Carlsberg-Laboratoriet*, **2**, 1879), and by Zopf (*Die Spaltpilze*, 1885, pp. 9 and 63).

The shorter rods and cells of *B. aceti*, when floating freely in culture fluid, are motile, but I have not noticed this property in the large abnormal forms.

When treated with dilute solution of iodine, *B. aceti* is stained yellow. Hansen states that the only difference between this ferment and *B. Pasteurianum* is that the latter is stained blue by similar treatment.

Boiling with dilute caustic potash quickly disintegrates the pellicle of *B. aceti;* also on treating it with strong sulphuric acid it is at once broken up, and the further addition of iodine merely turns it yellow.

Oxidation of Ethylic Alcohol.

Klein ("Micro-organisms and Disease," 1884), when describing *B. aceti*, states that "pure cultivations have not been made with it, and before deciding whether it is the real cause of the acetic acid fermentation, experiments with such pure cultures, *i.e.*, inoculations of alcoholic fluids with it, are required." For this reason, the first experiment I describe concerns this well-known action.

A litre flask half full of a 5 per cent. solution of pure ethylic alcohol in yeast water, and quite free from acid, was sterilised by the method described above. It was afterwards kept for 10 days at a temperature of 28° to be quite sure of its sterility. This being ascertained, the solution was inoculated with a trace of the pure cultivation of *B. aceti.* The flask was then placed on a hot water tray connected with a thermostat, and there kept at a constant temperature of 28°. On the second day after inoculation, a fine film of ferment had com-

menced to grow on the surface of the solution, which film increased in substance slightly during the next few days. On the tenth day, the flask was opened and found to smell strongly of acetic acid. 100 c.c. of the solution was distilled, pure water being frequently added to the retort, until the whole of the volatile acid had passed over. This volatile acid on titration gave a percentage of 1·021 acid calculated as acetic acid on the original 100 c.c. of solution distilled. The residue in the retort showed only 0·006 per cent. of non-volatile acid. There has been formed, therefore, during the growth of *B. aceti* in the original alcoholic solution, 1·021 per cent. of volatile acid and a mere trace of non-volatile acid. In order to ascertain the nature of the volatile acid, the rest of the solution was carefully distilled, and the very acid distillate neutralised with an excess of pure baric carbonate. After filtration, the whole of the solution was evaporated to dryness, and the residual salt dried at 130°. A weighed portion of the salt was decomposed in a platinum crucible by sulphuric acid, ignited, and the residual baric sulphate again weighed; on calculating, the following result was obtained:—

Per cent. of Ba in salt	53·65
,, of Ba in $Ba(C_2H_3O_2)_2$	53·73

showing conclusively that acetic acid was the one and only volatile acid formed in the above experiment with a pure cultivation of *B. aceti*.

The trace of non-volatile acid formed in the experiment seemed to answer to the tests for succinic acid, thus agreeing with Pasteur's observations; but the quantity found was too small for satisfactory identification. Traces of a body resembling aldehyde are generally found on distilling an acetic fermentation of *B. aceti*; this is more especially the case when the ferment is growing with an insufficient supply of oxygen.

Pasteur stated in his "Mémoire" that acetic acid is completely burnt to carbonic acid and water by *B. aceti*, when there is no alcohol in the solution. I confirmed this by the following experiment. A solution of 0·75 per cent. acetic acid in yeast water, sterilised as usual, was inoculated with *B. aceti*. The ferment grew with difficulty, and only formed an extremely thin pellicle on the surface of the liquid. After six weeks, the flask was opened and the acid determined. Only 0·25 per cent. of acid remained, showing that 0·5 per cent. of acid had disappeared during the growth of the ferment. A second flask, not inoculated, was found during the same time not to have lost any appreciable amount of acid. If an alcoholic solution is allowed to ferment until the whole of the alcohol is converted into acetic acid, I find that the acid so formed is much more quickly decomposed by

the ferment than in the experiment I have just described; this most probably is due to the strong pellicle of ferment formed during the time the oxidation of the alcohol was going on.

Action of B. aceti on Propylic Alcohol.

Seeing that ethylic alcohol is so freely oxidised by *B. aceti*, it appeared desirable to ascertain whether this action did not extend to the other alcohols of the same series. I first experimented on normal propylic alcohol, and prepared a solution containing 3 per cent. of the pure alcohol in yeast water. After sterilising, &c., in the usual way the solution was inoculated with *B. aceti*. For the first few days the ferment grew very slowly, but later a fine pellicle was developed on the surface. The flask was opened 14 days after inoculation, when the liquid was found to have a strongly acid odour. A sample taken for estimation of the total acid gave 1·20 per cent. calculated as $CH_3 \cdot COOH$. The rest of the solution was distilled, and the acid distillate neutralised with carbonate of barium, filtered and evaporated to dryness. After drying at 130°, a weighed portion of the salt was decomposed with sulphuric acid, ignited, and weighed. On calculation, the following result was obtained:—

Per cent. of Ba in salt	48·35
,, of Ba in barium propionate	48·41

showing that normal propylic alcohol is oxidised to propionic acid by the action of *B. aceti*, just as ethylic alcohol is oxidised to acetic acid. But a mere trace of non-volatile acid was found in the original solution after distilling off the propionic acid.

Action of B. aceti on other Alcohols.

The next experiments were made with methylic alcohol. I found this alcohol had to be purified by repeated distillation to get rid of all traces of resinous matter before the ferment would grow freely in its presence.

A 1 per cent. solution of this in yeast water was inoculated with *B. aceti*. In a few days the ferment was growing freely. On opening the flask after three weeks, the solution was found slightly *alkaline*. (Before going further I had better add that *B. aceti* grows freely in yeast water alone, the reaction becoming slightly alkaline. On distilling this solution, ammonia or ammonium carbonate distils over. The residue, after slightly acidifying with a few drops of sulphuric acid, yields a very small quantity of volatile acids which have a slight reducing action on silver nitrate and permanganate, and

which are probably a mixture of butyric with a little formic acid.) The alkaline distillate on examination contained only ammonia and methylic alcohol. The residue in the flask, after slightly acidifying with a few drops of sulphuric acid, was again distilled. A very small quantity of volatile acid was obtained, which had a slight reducing action on $AgNO_3$ and on $HgCl_2$, but the very small quantity of the acid and also its character is only what may be obtained from a fermentation of yeast water alone.

Another experiment was made on a solution of yeast water containing 1 per cent. of methylic alcohol and some calcic carbonate. This fermentation was allowed to go on for four weeks, during which time the ferment grew very freely. On opening the flask and distilling, after slightly acidifying with sulphuric acid, only 0·008 per cent. volatile acid was found. From the above two experiments, it is evident that *B. aceti* is unable to oxidise methylic alcohol to formic acid, under circumstances in which it acts freely on ethylic and propylic alcohols. But as it was possible that methylic alcohol might have been oxidised directly to carbonic acid and water in the experiments quoted, a flask containing 500 c.c. of yeast water was sterilised, and afterwards exactly 5 c.c. of methylic alcohol, sp. gr. 0·8151, was added, and the solution inoculated with *B. aceti*. In order that the alcohol in the solution should not be lost by diffusion of its vapour through the cotton-wool plug, the mouth of the flask was closed by an india-rubber stopper pierced by two tubes, so arranged that filtered pure air could be drawn through the flask every second day, the air that came from the flask being passed through a chloride of calcium tube to arrest any methyl alcohol that might be with it. The ferment in this experiment grew with great freedom, and the fermentation was allowed to go on for four weeks and a half. On opening the flask, the solution was carefully distilled until all the alcohol had passed over, and the sp. gr. of the distillates was taken. On comparing these weights with a table, I found 4·90 c.c. of alcohol had distilled over, against the original 5·00 c.c. with which the experiment had been started. These results agree as closely as could be expected considering the method used, and leave no doubt that, under the circumstances of my experiment, methylic alcohol is not acted on in any way by *B. aceti*. Why this should be so with an easily oxidisable liquid like methylic alcohol, when ethylic and propylic alcohols are acted on so readily, it is difficult to say. It can hardly be because the products of the action of *B. aceti* on methylic alcohol are poisonous to itself, for if so, why should it thrive so well in the presence of the alcohol?

I have made repeated attempts to oxidise isoprimary butylic

alcohol (b. p. 108°) by means of *B. aceti*, but have been unsuccessful, although the ferment will grow feebly in 0·5 per cent. solution of this alcohol in yeast water.

I have not succeeded in making *B. aceti* grow at all in presence of amylic alcohol (fermentation alcohol).

Action of B. aceti on the Carbohydrates.

In the *Comptes rendus* of March, 1878, p. 605, is a paper by Boutroux entitled "Sur la fermentation lactique," in which the author describes, as a continuation of Pasteur's work on the lactic ferment (*Ann. Chim. Phys.*, 1857), a purified cultivation of this ferment, which grows as a pellicle on the surface of solutions containing sugar and nitrogenous matter, and had the power of converting this sugar into lactic acid. He further finds that this ferment has the power of converting alcohol into acetic acid, and concludes that the lactic and acetic ferment are one and the same organism.

In the *Comptes rendus* of July, 1880, p. 236, another paper from Boutroux appears correcting his former conclusions, and stating that the acid formed by his ferment from sugar is not lactic but gluconic acid. He gives analyses of the acid and its salts, and further states that the ferment which forms gluconic acid is *Mycoderma aceti*, and that he was in error in calling it lactic ferment.

It appeared desirable to repeat this experiment with my pure cultivation of *B. aceti*. Boutroux in his experiments grew the ferment in a solution of glucose in yeast water containing a quantity of calcic carbonate to neutralise the acid when formed;* but as there is in this case a considerable quantity of organic matter from the yeast present which might possibly complicate the reaction, I preferred to make my experiments with solutions containing merely dextrose, and inorganic salts of known composition to serve as food for the ferment. For this purpose, I prepared a flask containing 3 litres of a solution composed of 2 per cent. dextrose dissolved in Pasteur's mineral solution, and to this 10 grams of pure calcic carbonate was added. This solution was sterilised, and after being kept as usual was inoculated with *B. aceti* on August 2nd. The ferment grew more slowly than in yeast water and dextrose, and the pellicle formed on the surface was extremely thin. On September 10th, most of the calcic carbonate having been dissolved, the flask was opened for examination.

* This acid fermentation of dextrose goes on freely in a solution without $CaCO_3$ being added; but when about 0·4 per cent. acid (calculated as $CH_3 \cdot COOH$) is formed, further action is much retarded.

A portion of the solution was distilled and examined for ethylic alcohol, but none was found. The residue in the retort was then rendered slightly acid with sulphuric acid, and the solution again distilled. The distillate gave no acid reaction, showing the absence of acetic and other volatile acids.

The bulk of the original solution was then filtered as clear as possible, and evaporated slowly to a small bulk. To this solution, a large excess of alcohol of 0·83 was added, which produced a bulky precipitate of a brownish gummy nature. After allowing the whole to stand 24 hours, the bright alcoholic solution was poured off, and a small quantity of water added to the precipitate, which dissolved it completely to a dark brown solution. After decolorising with animal charcoal, a large excess of alcohol was again added; this brought down the precipitate in nearly white flocks. The solution was allowed to stand until quite bright, and then filtered. After washing the precipitate thoroughly with alcohol and well draining, the salt was again dissolved in water, and the solution heated to 100°. Boiling alcohol was then added so as just to produce a slight permanent milkiness, and the solution was put on one side to cool slowly. After 48 hours, the bottom and sides of the beaker were covered with beautifully white roundish concretions, evidently of a crystalline nature. Under the microscope they were found to be masses of minute acicular crystals.

After drying this salt at 100°, two estimations of the CaO in it were made, giving—

No. I. 12·63 per cent. CaO.
No. II. 12·68 ,, ,,

Calcic gluconate, according to Hertzfeld's formula (*Annalen*, **220**, 335), $(C_6H_{11}O_7)_2Ca + 10H_2$, contains 12·50 per cent. CaO.

0·6454 gram of this salt was burnt with lead chromate and potassic dichromate. This combustion gave 0·3122 gram CO_2 and 0·7535 gram OH_2. On calculation, the Ca being taken as the mean of my two analyses, we get the following result:—

	Found.	$(C_6H_{11}O_7)_2Ca + 10H_2$.
C	31·84	32·14
H	5·37	5·36
O	53·75	53·57
Ca........	9·04	8·93

The above analyses leave no doubt that the salt with which we are dealing is calcic gluconate.

This salt does not reduce Fehling's solution, neither has its solution any action on polarised light. It reduces silver nitrate with

great ease, and also prevents the precipitation of ferric oxide by ammonia. Its aqueous solution, on being freely exposed to the air for several weeks, gradually deposits the crystalline form of the salt again, unchanged. On heating the dry salt strongly, it intumesces in a remarkable manner, and finally burns to a white ash. I have prepared the free acid from the calcic salt; and the solution of the free acid when evaporated in a vacuum leaves it as an uncrystallisable, glassy, nearly colourless mass. Its aqueous solution is intensely acid to the taste when concentrated, and on heating, even below 100°, it begins to turn brown and decompose.

In my fermentation experiment with dextrose, calcic gluconate appeared to be the only soluble calcic salt present. I therefore examined the insoluble residue from the fermentation, but found it to consist of calcic carbonate and cells of *B. aceti* alone. It therefore appears that the sole product of the action of *B. aceti* on dextrose is gluconic acid. If we consider dextrose, as it is generally taken, to have the constitution of an aldehyde of the hexhydric alcohol, mannitol, the reaction would probably be represented thus:—

$$\underset{\text{Dextrose.}}{\left\{\begin{array}{l} CH_2{\cdot}OH \\ CH{\cdot}OH \\ CH{\cdot}OH \\ CH{\cdot}OH \\ CH{\cdot}OH \\ COH \end{array}\right.} + O = \underset{\text{Gluconic acid.}}{\left\{\begin{array}{l} CH_2{\cdot}OH \\ CH{\cdot}OH \\ CH{\cdot}OH \\ CH{\cdot}OH \\ CH{\cdot}OH \\ COOH \end{array}\right.}$$

Gluconic acid being the sole product of the oxidising action of *B. aceti* on dextrose, considerably strengthens the idea of the constitution of dextrose being partly aldehydic, as represented in the above formula.

B. aceti on Sucrose.

My next experiments were made to ascertain what effect *B. aceti* might have on solutions of cane-sugar or sucrose. Having failed to make the ferment grow in solutions of cane-sugar and Pasteur's mineral medium, I prepared and sterilised a solution of yeast water containing 4 per cent. of cane-sugar, and inoculated it with *B. aceti* as usual. In a few days, the ferment was growing strongly. After six weeks, the flask was opened and the solution examined. It was found to be perfectly free from acid, and did not reduce Fehling's solution.

Another experiment was made in which the polarising power of the solution was noted previous to inoculation. After *B. aceti* had grown freely in the solution for three weeks, the flask was opened. The

contents were carefully made up to the original volume and filtered. On examining the solution with the polariscope, the original angle was obtained. A blank experiment made with the same yeast water and inoculated at the same time, showed that both before and after the growth of *B. aceti* there was no action on polarised light. The cane-sugar solution in my second experiment had a slight alkaline reaction, and did not reduce Fehling's solution; but on treating it with dilute sulphuric acid and warming, it reduced freely.

The above experiments show that *B. aceti* is unable to break up or change the molecule of cane-sugar.

Now if the constitution of cane-sugar is really aldehydic, as it is usually represented in the formula $O\begin{cases} C_5H_6(OH)_4\cdot COH \\ C_5H_6(OH)_4\cdot COH \end{cases}$, it appears strange that *B. aceti* is unable to attack the aldehyde part of the molecule in this case, in the same way that it acts upon dextrose when oxidising it to gluconic acid.

Action of B. aceti on Mannitol.

After my previous experiments, it appeared very desirable to study the action of the ferment upon mannitol, the alcohol corresponding to the aldehyde dextrose on which the ferment acts so freely.

Gorup-Besanez (*Ann. Pharm.*, **118**, 273), on oxidising mannitol by means of platinum black, found that mannitic acid, mannitose (a fermentable sugar), and an unfermentable gummy substance were the chief products. Mannitic acid he analysed and described, but he was unable to separate mannitose from the gummy product. He describes mannitose as not producing the least deflection of the plane of polarisation, but as reducing Fehling's solution freely.

Berthelot (*Ann. Chim. Phys.*, **50**, 369) states that by fermenting a 10 per cent. solution of mannitol in water, in contact with certain animal membranes, a "glucose" is sometimes formed. The results are very irregular, the "glucose" found varying from a mere trace to a tenth of the amount of mannitol used, the highest result obtained. The "glucose" could not be obtained pure, but Berthelot describes it as uncrystallisable, very soluble in alcohol, fermentable, as reducing Fehling's solution, and probably lævorotatory. The animal membrane used in the experiment is thought to be the cause of conversion of mannitol into sugar (?).

A. Fitz (*Ber.*, **9**, 1352) states that during the schizomycetic fermentation of mannitol, normal butyl and ethyl alcohols, and butyric and lactic acids are formed.

Hecht and Iwig (*Ber.*, **14**, 1760), by the oxidation of mannitol by alkaline potassium permanganate, obtained formic, oxalic, and a small

quantity of tartaric acid, and also a sugar which reduces Fehling's solution, and is probably mannitose.

F. Dafert (*Ber.*, **17**, 227) states that the products of the oxidation of mannitol vary according to the agent used, and also the time and temperature of oxidation. Carbonic anhydride, water, formic, mannitic, saccharic, tartaric, and probably glycollic acids have been observed; also a mannitose-like substance, and a sugar, mannitose, are invariably formed. Mannitose reduces Fehling's solution, and is optically inactive.

My first experiment on the oxidising action of *B. aceti* upon mannitol was made with a 2 per cent. solution of the latter body (Pasteur's mineral medium and a little gelatin being added as food for the ferment). After inoculation with *B. aceti*, the ferment grew freely. In six weeks' time, the fermented solution was examined. No acid had been formed, but the solution had acquired a very sweet taste and reduced cupric oxide freely, a result which pointed to some sugar having been formed from the mannitol during fermentation.

In order to separate this substance, the solution was evaporated on a water-bath and the residue exhausted with boiling alcohol, sp. gr. 830. The part undissolved by the alcohol consisted chiefly of gelatin, and possessed no cupric oxide reducing power. The hot alcoholic solution (which reduced Fehling's solution freely), on cooling, deposited some crystals of unaltered mannitol; these were filtered off, and the clear solution evaporated. A brown, very sweet syrup was left, which was treated with hot absolute alcohol, in which it dissolved completely, but on cooling a trace of mannitol and a little gummy matter were deposited. The clear solution was separated from this deposit and evaporated. After completely expelling all the alcohol from the syrupy residue, it was dissolved in water and decolorised by animal charcoal. A colourless, very sweet solution was thus obtained. On examining with the polariscope, the matter in solution was found to possess an $[\alpha]_j = -72{\cdot}0$, whilst the cupric oxide reducing power was found to equal $\kappa_{386}75{\cdot}23$. On adding a little yeast to the solution, it fermented slowly, and in a few days all its optical activity had disappeared, but the unfermented residue still reduced Fehling's solution slightly.

It is evident from the above experiment that during the growth of *B. aceti* in a solution of mannitol, a fermentable sugar is formed, possessing a high lævorotatory power together with a high cupric oxide reducing power. Lævulose is the only sugar at present known that possesses these properties.

In order to study this interesting reaction more closely, a solution was prepared containing 25 grams of mannitol in 1 litre of yeast water. After sterilisation and inoculation with *B. aceti* as usual, the

fermentation appeared to go on more briskly than in my first experiment. At the end of five weeks, when the flask was opened for examination, the solution contained no free acid. After evaporating the solution to a syrup, at a temperature of 70°, it was treated with alcohol as in my first experiment. No mannitol, however, was found, showing that the whole 25 grams had been decomposed during the fermentation. The brown syrup, purified as in my first experiment by absolute alcohol, was further treated with cold methylic alcohol, sp. gr. 816. In this, however, it was completely soluble. After evaporating this solution to expel the alcohol, the syrup remaining was dissolved in water and decolorised by animal charcoal as before. The optical activity and the cupric oxide reducing power were then determined with the following result:—

$$[\alpha]_{j386} = -86{\cdot}07$$
$$\kappa_{386} = 86{\cdot}11$$

In this experiment, therefore, the proportion of the rotatory power to the cupric oxide reducing power is much the same as in my first experiment, but the actual amount of lævorotary sugar is much greater.

In order to see if the sugar (presumably lævulose) which we have here could be further purified, a solution of the syrup was made in alcohol 820 sp. gr., and then excess of ether was added so as to fractionally precipitate the substances in solution. Three fractions were thus obtained, and the cupric oxide reducing power and optical activity were determined in each, with the following results:—

$$\text{1st Fraction}\ldots\begin{cases}[\alpha]_{j386} = -83{\cdot}6\\ \kappa_{386} = 87{\cdot}3\end{cases}$$
$$\text{2nd Fraction}\ldots\begin{cases}[\alpha]_{j386} = -89{\cdot}98\\ \kappa_{386} = 88{\cdot}86\end{cases}$$
$$\text{3rd Fraction}\ldots\begin{cases}[\alpha]_{j386} = -97{\cdot}49\\ \kappa_{386} = 97{\cdot}35\ (?).\end{cases}$$

These experiments point very strongly to the conclusion that the sugar that has been formed from mannitol is *lævulose*, the last fraction especially having a rotatory power closely approximating to the supposed rotatory power of pure lævulose, viz., $[\alpha]_j -106$.

I next endeavoured to ascertain the true rotatory power and cupric oxide reducing power of the lævulose by means of a fermentation experiment. The cupric oxide reducing power and rotatory power of a solution of the sugar of known specific gravity were carefully determined and the solution was then fermented, precautions being taken to prevent loss of alcohol. After fermentation, the alcohol was distilled, and the proportion of sugar decomposed was calculated from the alcohol found (Pasteur's figure 48·5 grams alcohol = 100 grams

$C_6H_{12}O_6$ sugar being used in this calculation). After determining the rotatory power and reducing power of the residue from the fermentation, the $[\alpha]_{j386}$ and κ_{386} of the fermented sugar were calculated from the figures thus obtained, with the following result:—

$$[\alpha]_{j386} = -99{\cdot}8 \text{ at } 15{\cdot}5° \text{ C.}$$
$$\kappa_{386} = 94{\cdot}26$$

Owing to at least one doubtful factor having to be used in the above calculation (viz., the proportion of alcohol equal to sugar fermented, which is unknown for lævulose), the figures just given cannot be considered to represent with great accuracy the $[\alpha]_j$ and κ of the lævulose from mannitol. Although these figures differ slightly, therefore, from those usually assigned to the lævulose from invert sugar (viz., $[\alpha]_j - 106$ and $\kappa = 100$), there is little or no doubt that the two lævuloses are identical.

The following properties of the lævulose from mannitol, which agree exactly with the properties of lævulose both from inulin and invert sugar, most strongly confirm this idea.

At ordinary temperatures, the sugar is a colourless, very sweet syrup, quickly turning brown when heated at 100°. It is slightly soluble in absolute alcohol in the cold, but on heating dissolves freely. On cooling the solution so formed, the sugar again falls out as a syrup; on further cooling below 0°, the syrup solidifies and becomes opaque, but so far I have not been able to obtain crystals of either this sugar or the sugar from inulin, after the manner described by Jungfleisch and Lefranc (*Compt. rend.*, **93**, 547). On treating an aqueous solution of the lævulose from mannitol with calcic hydrate, according to Dubrunfaut's process, a pasty mass of microscopic crystals of a lime salt is formed resembling exactly that obtained with the lævulose of invert sugar.*

After completely fermenting aqueous solutions of the lævulose from mannitol, there is always a small unfermented residue left which has no perceptible action on polarised light, but reduces cupric oxide. An estimation of its reducing power after allowing for products of fermentation left in solution, gave $\kappa_{386} = 33{\cdot}4$. The proportion of this compound to the lævulose in the syrup from a mannitol fermentation varies, but is generally about 15 per cent. How far it has been formed during the original fermentation, or how far from the decomposition of lævulose during evaporation of solutions, &c., is doubtful.

The experiments I have described show that mannitol is completely oxidised by *B. aceti*, and that the main product formed is lævulose.

* Since writing the above, I have converted lævulose from mannitol into mannitol again by means of sodium amalgam. Lævulose both from inulin and from invert sugar is converted in a similar manner into mannitol.

In its action upon mannitol, therefore, *B. aceti* behaves differently from all other oxidising agents which have been described (see above). Previous investigators have always found a small quantity of a sugar amongst the products of oxidation of mannitol, but this sugar is an optically inactive one, mannitose.

If the constitution of lævulose be represented by the formula which Kiliani (*Ber.*, 18, 3066) has recently shown to be probably the correct one, the following will perhaps represent the action of *B. aceti* upon mannitol:—

$$\underset{\text{Mannitol.}}{\left\{\begin{array}{l} CH_2{\cdot}OH \\ CH.OH \\ CH{\cdot}OH \\ CH{\cdot}OH \\ CH{\cdot}OH \\ CH_2{\cdot}OH \end{array}\right.} + O = \underset{\text{Lævulose.}}{\left\{\begin{array}{l} CH_2{\cdot}OH \\ CH{\cdot}OH \\ CO \\ CH{\cdot}OH \\ CH{\cdot}OH \\ CH_2{\cdot}OH \end{array}\right.} + OH_2.$$

In my experiments, one fact is very noticeable, viz., that no acid is formed during the decomposition of mannitol. Fermentations left for a month after the complete disappearance of all the mannitol showed no trace of acid. From this it was evident that the lævulose formed could not be further oxidised by the ferment to gluconic acid in the same way as dextrose. Experiments made by growing *B. aceti* in solutions containing lævulose prepared from inulin showed that this sugar also was not oxidised by the ferment. This in itself is evidence that there must be a very considerable difference between the molecular constitution of lævulose and dextrose, and appears to strengthen the theory that the one is a ketonic compound, and the other aldehydic. Thus,

$$\text{Lævulose..}\left\{\begin{array}{l} CH_2{\cdot}OH \\ CH{\cdot}OH \\ CO \\ CH{\cdot}OH \\ CH{\cdot}OH \\ CH_2{\cdot}OH \end{array}\right\}\begin{array}{c}\text{Not oxidised by} \\ \textit{B. aceti}.\end{array}$$

$$\text{Dextrose}\left\{\begin{array}{l} CH_2{\cdot}OH \\ CH{\cdot}OH \\ CH{\cdot}OH \\ CH{\cdot}OH \\ CH{\cdot}OH \\ COH \end{array}\right\}\begin{array}{l}\text{Oxidised by} \\ \textit{B. aceti}\text{ to}\end{array}\left\{\begin{array}{l} CH_2{\cdot}OH \\ CH{\cdot}OH \\ CH{\cdot}OH \\ CH{\cdot}OH \\ CH{\cdot}OH \\ COOH \end{array}\right\}\text{Gluconic acid.}$$

As we know now that by means of *B. aceti* we can convert mannitol into lævulose, it follows that dextrose can be converted into lævulose through this reaction, by first transforming it into mannitol by means

of sodium amalgam, *always supposing that the mannitol so formed is identical with that from manna.*

I think the experiments just described will be of interest to biologists, as well as chemists, as they help to show that the vital functions of certain organised ferments are most intimately connected with the molecular constitution of bodies upon which they act.

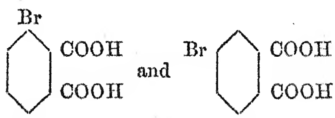
My best thanks are due to Mr. Horace T. Brown, and to Dr. G. H. Morris for help given me in various ways whilst pursuing this investigation.

XX.—*The Monobromophthalic Acids.*

By G. STALLARD, M.A.

Two monobromophthalic acids have been hitherto described, the first obtained by Faust (*Annalen*, **160**, 62) by the action of bromine and water on phthalic acid at 180—200°, the second by Guareschi, Meldola, and Smith, by the oxidation of certain bromo-derivatives of naphthalene. The first acid and its anhydride are said to melt at 138—140° and 60—65° respectively, the second at 174—176° and 133—135° respectively.

The two theoretically possible monobromophthalic acids are represented by the formulæ —



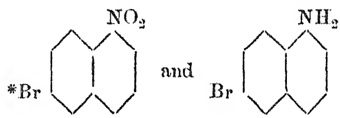
I. and II.

Faust's acid is supposed to correspond to formula I on the strength of an observation of H. v. Pechmann's (*Ber.*, **12**, 2126) that this acid can by a series of processes be converted into erythroxyanthraquinone. Both Guareschi and Meldola accordingly assume that the acid melting at 174—176°* is that represented by the second symbol. The force of these assumptions is, however, much diminished by the fact that the action of bromine and water on phthalic acid, according to v. Pechmann, gives rise to both the theoretically possible mono-

* Carnelley (*Chem. Soc. Trans.*, 1885, 591) also describes a bromophthalic acid obtained by the oxidation of a bromoditolyl, and which, though it melts at 203°, he regards as identical with Guareschi and Meldola's acid.

bromophthalic acids, and that he confessedly obtained his erythroxy-anthraquinone from a mixture of these acids, not having succeeded in separating them from one another.

Now Guareschi (*Annalen*, **222**, 292 and 298) obtained the monobromophthalic acid melting at 174—176° by oxidation, first, of a bromonitronaphthalene, $C_{10}H_6Br,NO_2$, obtained by the action of bromine on nitronaphthalene in molecular proportions, and, secondly, by oxidation of the corresponding bromonaphthylamine, $C_{10}H_6Br \cdot NH_2$. He therefore assumes that the constitution of these compounds is correctly represented by the symbols



in other words that the bromine-atom enters the second "ring" in a β-position.

I have recently prepared these compounds (each of which is undoubtedly a single substance, and not a mixture of isomerides) according to Guareschi's directions, and found that they possess the melting points and other properties assigned to them by that author; and with the view of throwing light upon their constitution, and that of the bromophthalic acid related to them, have made the following experiments.

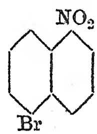
The bromonaphthylamine was converted in the ordinary way into the diazo-sulphate, and this was decomposed with absolute alcohol. The alcohol was then distilled off, and the sulphonic acid obtained subjected to steam distillation, the temperature of the liquid being kept at 135—140°. The slightly yellow oil thus obtained was unaltered in appearance by a second steam distillation, had a sp. gr. of 1·5, did not solidify at − 15°, and proved to be α-bromonaphthalene. Nothing further was obtained by even a very considerable rise in the temperature at which the steam distillation was effected.

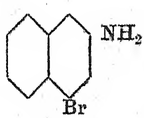
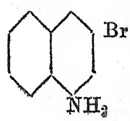
To another portion of the diazo-sulphate excess of bromine-water was added, and the flocculent orange precipitate of diazo-perbromide was warmed with glacial acetic acid till evolution of nitrogen ceased. From the acetic acid solution, a small quantity of water precipitated a substance which, after solution in slightly diluted alcohol with the addition of animal charcoal, gave fine brilliant needles of a dibromonaphthalene melting at 130—130·5°. Water was then added to the

* I omit, in this and similar cases, the alternative formula, since chemists have at present no means of ascertaining by which of two such symbols a given body is more correctly represented.

acetic acid mother-liquor as long as a precipitate was formed; this fraction proved to be identical in composition and melting point with the first.

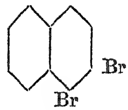
This dibromonaphthalene crystallises also in needles from glacial acetic acid, and appears to be identical, in spite of the difference in crystalline form, with the so-called γ-dibromonaphthalene obtained by Jolin by distilling α-dinitronaphthalene with phosphorus pentabromide, and found by Guareschi and Magatti among the products of the action of two molecular proportions of bromine on naphthalene; it is also probably identical with the compound melting at 126—127°, obtained in the form of microscopic needles by Därmstadter and Wichelhaus (*Annalen*, **152**, 303) by the action of 1 mol. of bromine on α-$C_{10}H_7 \cdot SO_3H$.

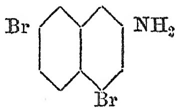
It appears, therefore, that this dibromonaphthalene contains, as has long been supposed to be the case, its two bromine-atoms in α-positions, and one in each nucleus, since the isomeric β-dibromonaphthalene (m. p. 81°), which also has its bromine-atoms in α-positions, contains them in the same nucleus. If this be so, Guareschi's bromonitronaphthalene must have a similar constitution, which may be expressed by the formula , and the bromophthalic acid melting at 174—176° must have its bromine-atom in the position contiguous to the two carboxyl-groups. This view is confirmed by a recent paper of Krüger's (*Ber.*, **18**, 1755), in which he shows that the anhydride of the monochlorophthalic acid obtained by the oxidation of the 1 : 2 : 3 monochlorortho-xylene has a much higher melting point than that from the isomeric 1 : 2 : 4 derivative of the same hydrocarbon. On the other hand, it must be admitted that Meldola's experiments (Trans., 1885, 511—515) favour a view exactly opposite to that here suggested as to the constitution of the monobromophthalic acids. This author, by bromination of the two bromonaphthylamines of the formulæ

 and ,

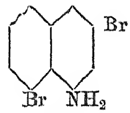
I.

has obtained two dibromonaphthylamines, giving on hydrolysis the same dibromonaphthalene (m. p. 75°), which is, therefore, an α-β-modification. The bromine-atoms, moreover, must be in different

nuclei, since the formula  is already assigned with good reason to the compound described by the same author in the Trans., 1883, 5. The dibromonaphthylamines in question are, therefore, represented by the formulæ


I.

and


II.

respectively.

The first of these gives on oxidation (according to Meldola) the bromophthalic acid melting at 174—176°; from the second he failed to obtain a bromophthalic acid, and unless we suppose that during the oxidation process an atomic migration occurs, it necessarily follows that the usual assumption as to the constitution of the bromophthalic acids is correct.

It appears, however, that in the oxidation of naphthalene-derivatives there may be, and in some cases probably are produced, owing to secondary actions, substituted phthalic acids other than those which might naturally be expected. If this be so, it is necessary to receive with caution a formula for a naphthalene-derivative based upon the results of an oxidation experiment, and a far safer method than that commonly used in oxidising haloïd substitution derivatives of this hydrocarbon would appear to be that adopted by Claus (*Ber.*, **15**, 320) in the case of ε-dichloronaphthalene, viz., to perform the experiment in presence of silver nitrate with the view of preventing secondary action.

XXI.—*Some Derivatives of Thiocarbamide.*

By George McGowan, Ph.D., F.R.S.E, Demonstrator in Chemistry, University College, Bangor.

In continuation of my work on the derivatives of methylsulphonic acid (*J. pr. Chem.* [2], **30**, 280), I studied at the suggestion of Herr O. Loew (in a private letter written after his having read the paper just mentioned) the action of thiocarbamide on trichloromethyl-

sulphonic chloride, $CCl_3 : SO_2Cl$, and from this I have been led on to investigate certain thiocarbamide compounds.

If the above-mentioned sulphonic chloride is added to an aqueous solution of thiocarbamide, no reaction takes place in the cold until after long standing, but, on warming, the chloride gradually dissolves, and sulphur is deposited. If, however, a cold or nearly cold solution of thiocarbamide in 80 to 90 per cent. alcohol is used, there is considerable development of heat on adding the chloride, and a mass of needles separates; the quantity of the latter being much increased by the subsequent addition of ether.

This compound was found to be identical with that obtained by Claus (*Annalen*, **179**, 139) by the action of chlorine on an alcoholic, or (with careful cooling) aqueous solution of thiocarbamide, viz., dithiocarbamide dichloride, $(CSN_2H_4)_2Cl_2$. In preparing it as above from trichloromethylsulphonic chloride, it is best to take quantities of the *pure* substances representing two molecular proportions of the sulphonic chloride and four of the thiocarbamide. The latter being dissolved in a small quantity of 90 per cent. alcohol, the chloride is gradually added, care being taken to avoid much rise of temperature. When the reaction is complete, an equal volume of ether is added, and, after the whole has stood for a short time, the dithiocarbamide dichloride may be collected and washed, first with a mixture of absolute alcohol and ether, and then with ether, and finally dried over sulphuric acid in a vacuum.

The compound thus prepared yielded the following results on analysis:—

(*a.*) 0·1590 gram gave 33·3 c.c. N at 16° and 770 mm. mercury pressure = 24·75 per cent. N.

(*b.*) 0·2841 gram ignited with copper oxide and lead chromate gave 0·1076 gram CO_2 and 0·0995 gram H_2O = 10·33 per cent. C and 3·89 per cent. H.

(*c.*) 0·3280 gram gave 0·1238 gram CO_2 and 0·1166 gram H_2O = 10·29 per cent. C and 3·95 per cent. H.

(*d.*) 0·1857 gram ignited with pure lime gave 0·2371 gram AgCl = 31·59 per cent. Cl.

	Calculated for $(CSN_2H_4)_2Cl_2$.	Found.	
H	3·59	3·89	3·95
C	10·96	10·33	10·29
N	25·10	24·75	—
Cl	31·83	31·59	—
S	28·70	—	—

A compound CSN_2H_3Cl would require 2·72 per cent. H.

The filtrate from the above dithiocarbamide dichloride contains another product crystallising in stellate groups of the finest needles, and having probably the composition $(CSN_2H_4)_2(CCl_3SO_2)_2$. This will be referred to in a future paper.

Under similar conditions, methylsulphonic and dichloromethylsulphonic chlorides, $CH_3{\cdot}SO_2Cl$ and $CHCl_2{\cdot}SO_2Cl$, yield the same product, as does also phosphorus oxychloride, $POCl_3$; * but I failed to obtain it with acetyl chloride.

As already described by Claus, the above dithiocarbamide dichloride crystallises in rather small colourless needles, readily soluble in water, less so in alcohol, and insoluble in ether.

If a small portion is dissolved in 90 per cent. alcohol on a microscopic slide, the compound separates out again (after the slow evaporation of the alcohol) in highly characteristic plates (monoclinic ?). It also crystallises in the same way from its cold aqueous solution, but in this case the plates are very much elongated and mixed with long needles.

In like manner, the dichloride, dissolved in water on a microscopic slide, gave—

(*a.*) With dilute nitric acid, a crystalline precipitate, the crystals being like jagged daggers or long sword-like leaves (see below).

(*b.*) With platinum tetrachloride, large thin rectangular crystals. I have not investigated this compound.

The very interesting reaction which this dichloride (or the corresponding dibromide) gives, on heating its aqueous or alcoholic solution, or on the addition of an alkali, has already been explained by Claus, according to the following equation :—

$$(CSN_2H_4)_2Cl_2 = 2HCl + S + \underset{\text{Thiocarbamide.}}{CSN_2H_4} + \underset{\text{Cyanamide.}}{CNNH_2},$$

or a derivative of cyanamide, *e.g.*, dicyandiamidin. He was unable to obtain the cyanamide free from thiocarbamide for analysis; however, exactly the same reaction has quite recently been observed by Verneuil (*Compt. rend.*, **100**, 1296), for the corresponding selenium compound, $(CSeN_2H_4)_2Cl_2$, which sufficiently corroborates his view.

Dithiocarbamide dichloride cannot be recrystallised from water or alcohol, as the solutions invariably deposit sulphur. An aqueous solution strongly acidified with hydrochloric acid may, however, even be heated with impunity, and in the cold the dichloride separates out

* This phosphorus oxychloride was not quite pure.

in large thin plates (similar to those on the microscopic slide mentioned above); but I have never, even in this way, been able to obtain it quite free from deposited sulphur. Hence the necessity of preparing it pure in the first instance. It is stable at ordinary temperatures.

Action of Dilute Nitric Acid on Dithiocarbamide Dichloride.

If, as already indicated, dilute nitric acid is added to a moderately concentrated aqueous solution of the dichloride, most characteristic colourless crystals separate at once, while the liquid is found to contain free hydrochloric acid. These crystals are almost insoluble in dilute nitric acid, more soluble in water (but still only sparingly), practically insoluble in cold absolute alcohol, and insoluble in ether. The compound is thus easily obtained pure by washing successively with water, alcohol, and ether, and drying over sulphuric acid in a vacuum.

These crystals were also observed to be formed in the mother-liquor from the preparation of thiocarbamide nitrate: CSN_2H_4,HNO_3 (formed by adding strong nitric acid to a concentrated aqueous solution of thiocarbamide), red fumes being at the same time evolved.

The pure compound gave the following results on analysis:—

(*a.*) 0·3783 gram gave 0·1228 gram CO_2 and 0·1064 gram H_2O = 8·85 per cent. C and 3·12 per cent. H.
(*b.*) 0·4097 gram gave 0·1232 gram CO_2 and 0·1138 gram H_2O = 8·20 per cent. C and 3·09 per cent. H.
(*c.*) 0·1496 gram gave 37·6 c.c. N at 12° and 771 mm. = 30·27 per cent. N.
(*d.*) 0·1510 gram gave 38·2 c.c. N at 11° and 766 mm. = 30·41 per cent. N.

	Calculated for $(CSN_2H_4)_2(NO_3)_2$.	Found.	
C	8·70	8·85	8·20
H	2·90	3·12	3·09
N	30·44	30·27	30·41

The nitrogen estimation (*d*) was made from a sample 10 days old. The two estimations of carbon and hydrogen were made from the same preparation.

Thiocarbamide nitrate, CSN_2H_4,HNO_3, requires 3·61 p. c. H.
A compound, $CSN_2H_3NO_3$, would require 2·19 p. c. H.
" $CSN_2H_3NO_2$, " 2·48 "

This somewhat peculiar compound is therefore *dithiocarbamide dinitrate*, $(CSN_2H_4)_2(NO_3)_2$.

A further confirmation of its composition is given by the filtrate (from the dichloride and dilute nitric acid) being found to contain much free hydrochloric acid, but not a trace of chlorine, thus :—

$$(CSN_2H_4)_2Cl_2 + 2HNO_3 = 2HCl + (CSN_2H_4)_2(NO_3)_2.$$

That this filtrate contains extremely little dinitrate in solution is easily proved by the addition of a solution of silver nitrate. First silver chloride is thrown down, and then only a very small quantity of a silver thiocarbamide compound.

The above dinitrate is comparatively stable, and therefore differs in this respect from thiocarbamide nitrate, as described by Reynolds (*Annalen*, **150**, 231). Possibly the extreme instability of Reynolds' compound may have been due to the presence of a small quantity of free nitric acid.

Although a good many samples of the dinitrate were prepared, and kept for months in tubes over calcium chloride, only one exploded, and that one almost immediately after preparation (I noticed that in this case the crystals were very small, *i.e.*, the compound was very finely divided). It appears to withstand a temperature of 60° for some hours with little or no decomposition, but decomposes gradually on being heated more strongly. When kept in a dry tube, decomposition goes on very slowly, hydrocyanic acid being evidently evolved and sulphur deposited. It separates from the dilute mother-liquor of its preparation in beautiful long columnar prisms. Like the dichloride, it at once deposits sulphur when its solution is heated or on the addition of an alkali to it.

A solution of potassium nitrate likewise precipitates at once a cold aqueous solution of dithiocarbamide dichloride. The crystals in this case are somewhat different in form; they are long well-developed prisms (possibly monoclinic), among them being many well-crystallised individuals. From dilute nitric acid the crystals are more agglomerated.

Action of the Chlorides of Iodine on Thiocarbamide.

If iodine monochloride, ICl, or trichloride, ICl_3, is added to a cold solution of thiocarbamide in alcohol, dithiocarbamide dichloride is formed, and iodine separates, even when the thiocarbamide is present in excess :—

$$2CSN_2H_4 + 2ICl = (CSN_2H_4)_2Cl_2 + I_2.$$

With a concentrated solution, or with powdered thiocarbamide moistened with alcohol, the action is very violent.

In aqueous solution, the iodine seems to separate more slowly, indeed in an aqueous solution containing an excess of thiocarbamide, a certain amount of iodine compound seems to remain undecomposed until the solution is heated (comp. Verneuil on the seleniothiocarbamide compounds, *Compt. rend.*, **100**, 1296).

Action of Potassium Iodide on Dithiocarbamide Dichloride.—If equivalent quantities of these (finely powdered) be shaken up together in absolute alcohol, they react as shown in the equation:—

$$(CSN_2H_4)_2Cl_2 + KI = 2KCl + 2CSN_2H_4 + I_2.$$

Here again the separation of iodine appears to go on more slowly if an aqueous solution is used.

Dithiocarbamide Di-iodide, $(CSN_2H_4)_2I_2$.

This can, however, be prepared by rubbing together in a mortar *pure* thiocarbamide and iodine in the proportions of their molecular weights, just sufficient alcohol being added to make a pasty mass. In this way the iodine is taken up, and a compound crystallising in long prisms formed. The reaction succeeds best with small quantities; for instance, 0·47 gram iodine and 0·28 gram thiocarbamide. The product is treated several times with cold benzene to remove traces of free iodine, and the nearly colourless residue is then dried between folds of filter-paper.

0·3528 gram gave 39·8 c.c. N at 12° and 768 mm. = 13·54 per cent. N.

$(CSN_2H_4)_2I_2$ requires 13·79 per cent.

When prepared, this di-iodide is quite stable and can be kept for any length of time in a dry tube. On being warmed it melts—at a comparatively low temperature—with liberation of iodine. It crystallises, as already mentioned, in long colourless prisms. There is some difficulty in getting good crystals for the microscope.

Benzene does not dissolve it, but water, alcohol, and ether do, with immediate separation of iodine, *which accounts for its not being formed in solution.* This decomposition of the di-iodide occurs even if it be dropped into absolute alcohol which has been cooled by a mixture of ice and salt, or on adding a drop of absolute alcohol to the di-iodide covered by a layer of benzene; chlorine and *concentrated* hydrochloric acid added to it likewise liberate iodine at once.

On heating the aqueous solution, or on addition of caustic alkali,

sulphur separates. *This separation of sulphur is therefore characteristic of the di- (chlor-, brom-, nitro-, &c.) derivatives of thiocarbamide.*

Dilute hydrochloric acid does not cause separation of iodine in the cold (indeed it seems insoluble in this and also in dilute nitric acid); on heating the mixture, however, iodine is liberated freely, but no precipitation of sulphur occurs. This shows that it is decomposed, under those conditions, more readily into iodine and thiocarbamide than into hydriodic acid, sulphur, thiocarbamide, and cyanamide (compare with the decomposition products of the dichloride or dibromide). Although the di-iodide appears to be insoluble in dilute nitric acid, still, if a drop of alcohol be added to a little of it on a microscopic slide, and then at once a drop of dilute nitric acid, the dinitrate is precipitated.

With regard to the action of cyanides on thiocarbamide and its dichloride, I need merely say at present that it appears to be impossible to prepare dithiocarbamide dicyanide, as this substance splits up immediately after formation. I hope, however, to go more fully into this point in a future paper.

University College of North Wales,
Bangor, December, 1885.

XXII.—*Bacteriological Research from a Biologist's Point of View.*

By E. Klein, M.D., F.R.S., Lecturer on General Anatomy and Physiology in the Medical School of St. Bartholomew's Hospital, London.

The memorable and classical researches of Pasteur on the relation of micro-organisms to various fermentative processes and to putrefaction have given an active impetus to investigations on the chemical activity of micro-organisms, and during the last 10 or 15 years a great number of facts have been brought to light, showing how enormous and important the *rôle* is that bacteria and yeasts play in the economy of nature (comp. Professor Frankland's paper, Trans., 1885, 159). A great deal of this knowledge is real, and has been proved to be so by numerous accurate experiments. Thus it has been shown beyond any doubt that alcoholic fermentation is caused by the multiplication and activity of the yeast, known as *Saccharomyces*, that acetic acid fermentation is produced by *Mycoderma aceti*, that lactic acid fermentation is produced by *Bacterium lactis*, and it is also known that putrefaction is caused by a variety of species of bacilli. A good deal, however, of knowledge obtained with regard to chemical processes produced by micro-organisms, although put forward as perfect, on close examination is found to be in a very imperfect state.

I will illustrate this by a few examples, which I could multiply. There can be no doubt that the complex process spoken of as putrefaction of proteïds is due to bacteria, but when we come to inquire which part of the process is due to which bacteria, we receive no definite answer. Putrefaction is a process by which proteïds undergo changes, beginning with the formation of peptones, leading then to the formation of leucine and tyrosine, of indole, skatole, phenol, and a variety of substances belonging to the aromatic series, and further of certain alkaloïds known as ptomaïnes, ammonia and its salts, and nitrates, with the simultaneous development of sulphuretted hydrogen. Now no one has yet shown whether this whole series of changes is due to one kind of organism, or whether one kind of organism commences the process, and it is then carried on a step further by another kind of organism. We have certain well-established experiments by which it is shown that a certain kind of organism produces the change of sugar into alcohol, that is, the *Saccharomyces cerevisiæ*. After this has finished converting sugar into alcohol, another organism steps in and changes the alcohol into acetic acid. It is probable

that a similarly complex process occurs in putrefaction, that is to say, it is probable that one set of organisms only brings the proteïds down to a certain stage, preparing as it were the ground for another set which then begin their activity.

Another illustration which I can give of the imperfect state of our knowledge is this. The ammoniacal fermentation of urine, consisting as you all know in the conversion of urea into ammonium carbonate, is according to the account given by Pasteur and Cohn, due to a micrococcus called the *Micrococcus ureæ*. Professor Frankland told you in his address (*loc. cit.*, p. 178), that he found in ammoniacal urine a kind of vibrio which he considers to be the ferment of the ammoniacal change. Now I have myself examined a great many samples of urine that have undergone ammoniacal fermentation, but I have not found this vibrio. Had Professor Frankland isolated this vibrio, and, having isolated it by pure cultivations, had he then produced with it the ammoniacal fermentation in sterile urine, we should have been able to say that his so-called *Bacillus ureæ* is also an active agent in the conversion of urea into ammonium carbonate; but not having done so, and merely finding it present in ammoniacal urine, the assertion that it is the cause of the ammoniacal fermentation is open to question. To illustrate, at the same time, how an investigation of this nature ought to be carried out in order to command absolute value, I will mention to you experiments which were conducted last year by Leube and Graser (*Virchow's Archiv*, **100**, 3). These gentlemen set themselves the task to determine which organisms produce the ammoniacal fermentation of urine. They proceeded in this way. They took ammoniacal urine, that is to say, urine after it had undergone ammoniacal fermentation, and isolated by careful experiments, in a way which I shall describe more minutely later on, the various bacteria present in such urine. Amongst the great variety of bacteria present, four kinds proved themselves capable of producing the ammoniacal changes of urea; first and foremost, a sort of straight bacillus, thick and rounded at its ends; secondly, a micrococcus identical with the known *Micrococcus ureæ*; the third, but of less pronounced activity, is a small short bacillus, oval in shape; whilst the fourth, still less active, is a very short bacillus, with truncated ends. These four kinds of organisms have been isolated, carried in pure cultivations through many successive generations, their morphological characters well ascertained, so that they might be recognised at once whether present or absent in a given cultivation; and with each species separately, sterile urine or sterile fluids containing urea were inoculated, and the chemical action of the several species studied.

To illustrate, on the other hand, an inconclusive experiment, I will

mention the following examples. We are told by Professor Frankland that, according to Bell, *Mucor racemosus* is capable of producing alcohol out of sugar, that is to say, that it is also an alcoholic ferment. Now as far as I am able to say, this *Mucor racemosus* has not been isolated by exact methods; all that has been ascertained is that *Mucor racemosus* has been sometimes found to be present where alcoholic fermentation has been going on. But if you come to inquire more carefully into the matter, you will find that besides *Mucor racemosus*, *Saccharomyces* has also been present, and one would say with little hesitation that it was the latter organism which produced the alcoholic fermentation, whilst the mucor was merely present accidentally. A few years ago, Dr. Kern (*Biologisches Centralblatt*, II), described a peculiar bacillus, which owing to its containing a spore at each end he named *Dispora*, and because it was found in fermenting milk, used in the Caucasus as a drink under the name of "kephir" or "hippö," it was termed *Dispora Caucasica*. Now of this *Dispora Caucasica* Kern maintained that it is the active ferment in this alcoholic fermentation. Why did he maintain that? Because he found it always present in fluids undergoing this fermentation. Later on he was able to isolate it by pure cultivations, and then he became convinced that this bacillus had nothing to do with the alcoholic fermentation, but that the real agent in this process is a *Saccharomyces;* consequently this *Dispora Caucasica* is merely an accidental concomitant of this particular process. Similar criticisms might be applied to the various organisms which have been mentioned as the causes of the butyric fermentation by Fitz and Bell. As far as at present known, Van Tieghem and Prazmowski's *Clostridium butyricum* is the real ferment in this process. Many of the assertions made as to organisms having caused certain chemical processes are therefore untrustworthy, because they are due to either of the following sources of error: first, working with non-sterilised material; and, secondly, not isolating the organisms and testing their activity. If of any organism it is to be said with something like certainty that it really is the active cause of a specific chemical process, it must be shown, first, that when obtained pure, that is, when isolated it possesses certain well-defined characters; secondly, when introduced in this pure state into a suitable material, it must set up the specific action. These elementary conditions of experimenting are thoroughly appreciated and employed by most pathologists at the present day in their investigations into the relation of disease germs, but I am afraid they have not yet been fully understood by chemical investigators.

I will describe to you the methods which pathologists employ in ascertaining whether a given disease is due to a certain organism.

In the first place, the pathologist does ascertain whether an organism and which organism is present in the diseased tissues. In a variety of ways he studies the characters of such an organism by fresh examination, by methods of staining with various dyes, and by cultures. By this latter method, he not only studies their behaviour in various culture media, but at the same time isolates the organism in order to obtain pure cultivations. Having then obtained unmistakably pure cultivations, he proceeds to inoculate with them suitable animals, and ascertains whether this purified organism is capable of again producing the same disease from which it had originally been derived. And, further, in this so induced disease, the same organism must again be detected; by morphological study, and by the method of culture, it must become clear that in this new infection we meet with exactly the same organism as in the original disease.

I shall describe to you then, first, the method of cultivation and isolation, and, secondly, the method of testing the activity of the purified organism.

Supposing we have to do with the disease known as malignant anthrax: in this disease, the blood is the soil or locality in which the *Bacillus anthracis* finds its most suitable conditions for active growth and multiplication. The blood of an animal dead or dying of malignant anthrax very often contains vast numbers of this *Bacillus anthracis*. Every droplet of such blood inoculated into a suitable animal produces with certainty malignant anthrax and death in this animal. Its blood again teems with the *Bacillus anthracis*. But notwithstanding this we do not yet conclude that this *Bacillus anthracis* is the active ferment of this disease, because the *Bacillus anthracis* may be only an accidental concomitant; there may be another organised or non-organised ferment present, which is the real virus. In order to be able to say that the *Bacillus anthracis* is really the active virus, pathologists have found it necessary to isolate this *Bacillus anthracis* by cultivation. Koch was the first who achieved this cultivation. A drop of blood of an animal dead of anthrax, or a bit of the spleen of such an animal, was introduced into some suitable nourishing medium. He found that the *Bacillus anthracis* soon undergoes rapid multiplication by division, and that after a certain time, only hours sometimes, it formed in its interior bright oval seeds or spores. These spores were then introduced into fresh nourishing media, and they were seen to grow out or to germinate into bacilli, which rapidly multiplied by division. These bacilli, either after they had been forming spores, or before this period had been reached, were transferred to a fresh nourishing medium, in order to obtain a new crop of bacilli, and in this way by a number of successive cultivations he obtained the bacilli in a pure state, that is

to say, he obtained bacilli which had been far removed from their original nidus, *i.e.*, the blood. Now he found that however far removed cultures of the bacilli were, they always have the same action, namely, when introduced into a suitable animal, they invariably produce malignant anthrax and death, the blood and spleen of such animals containing vast numbers of the bacilli. In the same way, Koch proved that the bacillus known as *Bacillus tuberculosus* is the active agent of the pathological process known as tuberculosis.

Fehleisen proved by the same kind of experiments that a micrococcus is the real cause of erysipelas, and I could mention a number of other instances, *e.g.*, septicæmia and swine fever, and many others, where a definite infectious disease has been proved beyond any doubt to be caused by a definite species of organism.

In all these experiments of pure cultivations, the material in which the organism is to grow must at the outset be made sterile, for if by any chance another organism, say a septic organism, happens to be present at the outset, this will suppress the disease organism that is introduced. The sterilisation of nourishing materials is therefore the first and I may say an essential condition for the success of the experiment; and this—namely, the sterilisation of the nutritive material in which the given organism is to grow, and in which it is to be obtained in pure culture—must be the first attempt in all experiments coming under this head. The sterilisation of nutritive materials is always effected by heat. The same of course applies to all vessels, instruments, &c., used in connection with such nourishing materials, the vessels that are to contain the nourishing material and the instruments that are used for the putting in or taking out the organisms. If you have to deal with a given nourishing material, it is necessary after sterilisation, or after supposed sterilisation, to keep it under such conditions as would facilitate the development of organisms. If the material remains unaltered, and barren of organisms, under these conditions you are justified in saying that this material is free from any germs. Having ascertained that this is the case, you introduce your organism which you wish to test in its chemical activity. Of course you have to be careful to introduce only that one organism which is to be tested, that is to say, you have to be careful of accidental contamination with organisms that are not wanted. There is at present a tendency to neglect accidental contamination by organisms contained in the air. You see in many pamphlets, in some books also, that it is recommended when introducing a definite organism into fresh nutritive material, that is to say, when inoculating nutritive material with a given organism, to expose the nutritive material to the free access of air during inoculation. Now there is no doubt that at certain seasons, and at some

places, nutritive materials can be exposed to free access of air, of course for short periods, say seconds, without any actual contamination with air organisms taking place. But anyone who has worked at this kind of research at all seasons of the year, and in a variety of localities, must have found that the danger from accidental contamination with air organisms is a real one. Professor Tyndall has drawn attention in a masterly way to these dangers, and has proved that, however short the time may be during which suitable nourishing materials are exposed to free air, accidental contamination with septic organisms does take place oftener and to a larger extent than can be desired by those who are engaged in such work. In London, free exposure of suitable nutritive materials to air is followed in a certain percentage of cases by contamination with the following organisms: —foremost are the spores of moulds; then torula or saccharomyces: then micrococcus and the spores of bacilli.

The isolation of bacteria which happen to be present in a given fluid or solid is achieved in a variety of ways. The method which is now employed to a great extent is that of plate cultivation, first introduced by Koch. It is based on the fact that when a variety of organisms are introduced into nutritive gelatin, previously liquefied and distributed, by shaking, through this gelatin, after the gelatin is allowed to congeal, the different organisms are kept permanently in different places. Then the conditions under which the gelatin is placed are such that organisms can multiply, it is found that each one of those different organisms will give rise to a colony made up of members of its own kind. In this way, it can soon be ascertained which kind of organisms has been introduced, and even how many different kinds have been introduced, provided that the original number introduced is not too large, so that the different colonies making their appearance in the gelatin remain sufficiently isolated. This is practically the method which Dr. Angus Smith first used for the study of bacteria in water. The better plan is that adopted by Koch, namely, after the introduction of the bacteria mixture into the liquefied gelatin, the latter is poured out on glass plates or similar vessels, previously sterilised, and then kept in a closed moist chamber. The gelatin of course is allowed to set, and is kept in the solid state, that is to say, the temperature at which these gelatin plates are kept must not be higher than the temperature at which the gelatin remains solid. After a few days, a number of spots are formed on these plates, each spot corresponding to a colony; the different colonies, when due to different species, show different characters (size, colour, liquefaction or not of the gelatin, &c., &c.) already to the unaided eye. From such plate cultivation, pure cultures can be made by inoculating from any of these different colonies fresh nutritive material contained in flasks

or test-tubes, or any other vessel, of course the nutritive material having been previously sterilised. This is the simplest method of isolation, and the one at present the most employed. It has its drawbacks, and it has its great advantages. The drawbacks are chiefly these: first, accidental contamination with air organisms is not excluded. You may therefore obtain a number of colonies in your plate cultivations which have not been represented in the fluid from which you derived your bacteria. This may not count for much when you have to deal with the isolation of an organism the special characters of growth of which you have previously already ascertained, for you may easily see whether in the plate cultivation your organism has made its appearance, and it makes very little difference whether there are any others present, or how many, but it is of considerable importance when you are first searching for and ascertaining the existence of an organism the characters of which you do not yet know.

Another disadvantage of this method is that although many organisms are capable of growth in nutritive gelatin, such as is commonly used, there are other organisms, and some very important organisms, at any rate important to pathologists, which refuse to grow in gelatin. Again, there are other organisms which, although not incapable of growth in gelatin, will not grow in it, or far too slowly, at the temperature at which gelatin remains solid; they require much higher temperatures in order to develop into colonies that can be recognised by the unaided eye. These disadvantages apply also to water analysis by plate cultivations, such as have been minutely described and extensively used by Dr. Percy Frankland.

Another very good method of isolation is that by "dilution." In this method a given number of different bacteria are distributed over or in a large quantity of previously sterilised indifferent fluid, so that a definite quantity of this fluid contains only one organism. With this definite quantity of fluid nutritive material is inoculated, and then such nutritive material becomes the seat of the growth of that one kind of organism. This is the method which was first used by v. Naegeli, and afterwards with great success by Lister, in his investigations of *Bacterium lactis*.

A third method of isolation is that known under the name of "fractional cultivation," first used by Klebs. In this method the fact is made use of that different organisms grow to a different degree in different nutritive media. It is within the knowledge of everybody who has worked with bacteria, that different bacteria require different materials to grow in—some grow better than others in a given nutritive medium. Now supposing we have a fluid or a solid which contains, as the microscope proves, a variety of bacteria,

on inoculating with this mixture of bacteria one and the same kind of simple nutritive medium contained in several test-tubes, and exposing these to suitable conditions of growth, it will be found that after one or two days there is present in this particular nutritive medium the offspring, not of all the organisms that have been introduced, but pre-eminently and predominantly, perhaps, only those of one species. If that be the case, there is no difficulty in obtaining pure cultures from this one species, provided we use only a trace of this growth for the new cultivation. The chances are that by inoculating a trace of that growth into a fresh nutritive material of the same kind as above, we introduce only one species, because one species is only present predominately. Growing different bacteria in different media in this way, it is then found that they multiply or grow with different degrees of rapidity. In a similar way success may be achieved by adding to or subtracting from the nutritive medium certain substances.

In starting the cultivation of organisms, various methods are used for inoculation. There is Koch's method, by which a platinum wire, heated and subsequently cooled, is used to introduce the trace of the organism into nutritive gelatin or other material, contained in test-tubes, plugged with sterile cotton-wool. In this process, the cotton-wool plug is altogether removed. The test-tube containing the nutritive material, which is solid, is inverted, and then the inoculation is performed with the platinum wire by pushing the infected end of this wire into the solid material; the plug is replaced, the test-tube again put upright and exposed to the suitable conditions favouring the growth of the organism. In this process of inoculation, the chances of accidental contamination are of course not avoided. In the summer months, and in London, this method of inoculation is followed in a considerable percentage of cases by undesired accidental contamination.

I myself prefer the plan in which accidental contamination is reduced almost to *nil*. I take a pointed capillary pipette, freshly made, pass one end through the cotton-wool plug (previously drawn up halfway) down into the culture tube from which inoculation is to be made, allow a drop to ascend into the capillary tube, withdraw it, and pass it through the cotton-wool plug into the tube in which growth is to be started. In this way the chances of accidental contamination, owing to the lifting out of the plug, are reduced to the smallest dimensions, provided, of course, that the cotton-wool plug is sterile. By the plate cultivation, and by cultivations in test-tubes, the characters, both morphological and of the mode of growth, can be studied and ascertained; and it will be found that many different species have in this respect different characters. Some grow in spots, others in flat patches, others as films, uniform or com-

posed of minute droplets; some grow best in the depth, others best on the surface; some liquefy gelatin, others do not liquefy it, and so on.

Having, then, ascertained the characters of an organism, and obtained it in pure cultivations, the organisms are then tested for their activity by inoculating with them the suitable nutritive material. If this organism, by multiplication in this material, is capable of starting a specific chemical action in this new suitable material, then we are bound to say that it is this organism which is the cause of the specific action. The whole chain of evidence must be complete in the sense which I have indicated, in the sense in which it is considered as complete by pathologists of the present day, and only then, and not till then, will the statements put forward by chemists command that value which they claim. Not till chemists come to look upon the matter in the same light in which we look upon it, namely, to obtain the organisms pure, to render nutritive material sterile, to be able to produce with this pure organism the specific chemical activity you wish to obtain—not till you have fulfilled all these conditions, can you claim to have established the fact that a definite organism is the cause of a definite chemical process.

XXIII.—*On the Constitution of Undecylenic Acid, as indicated by its Magnetic Rotation, and on the Magnetic Rotation, &c., of Mono- and Di-allylacetic Acids, and of Ethyl Diallylmalonate.*

By W. H. Perkin, Ph.D., F.R.S.

Amongst the substances examined when first studying the subject of the magnetic rotation of compounds was undecylenic acid, an unsaturated acid of the formula $C_{11}H_{20}O_2$, discovered by Krafft (*Ber.*, **10**, 2035), as a product of the distillation of castor-oil under reduced pressure. The measurements of this substance were not given in the paper I had the honour of laying before the Society some time since, because they did not appear to be consistent with those I obtained for other unsaturated compounds. I was desirous of further considering them, as I felt sure that a careful study of the subject would clear up this apparent discrepancy.

Both the acid and its ether were examined. The acid was obtained from Kahlbaum, and purified by rapid distillation under reduced pressure. It boiled at 230—235° (corr.) at 130 mm. Krafft has

shown that it undergoes some amount of change, even when distilled under reduced pressure, so that the specimen cannot be considered quite pure. I find that this acid does not appear to undergo any alteration when dissolved in alkali and treated with sodium amalgam for two or three days. The acid examined was nearly white and beautifully crystalline. Its density when in the fused state was found to be as follows:—

$$d\frac{25^\circ}{25}\ 0\cdot91020,$$

$$d\frac{45^\circ}{45}\ 0\cdot89930.$$

The following numbers were obtained for its magnetic rotation:—

	t.	Sp. rotation.	Mol. rotation.
	26·5°	1·1153	12·534
	26·5	1·1157	12·537
	24·5	1·1174	12·541
	24·5	1·1209	12·575
Average	25·5	1·1174	12·547

Ethyl Undecylenate.—This substance was obtained by saturating an alcoholic solution of the acid with hydrochloric acid gas. The etherification takes place easily, so that it is not necessary to keep the product long in contact with the hydrochloric acid, which would probably be unadvisable as it is an unsaturated compound. The new ethereal salt was separated by the addition of water, and further purified by solution in ether, washing with sodium carbonate, drying over anhydrous potassium carbonate, and distilling. After fractioning a few times, it was obtained as a colourless oil, boiling at 263·5—265·5° (corr.).

Ethyl undecylenate is much more stable than the acid, and appears to undergo but little change when distilled. It has a peculiar fruity but not pleasant odour.

On analysis it gave the following numbers:—

0·1175 gram of substance gave 0·1200 gram of H_2O and 0·3156 gram of CO_2.

	Found.	Calc. for $C_{13}H_{24}O_2$.
C	73·25	73·11
H	11·37	11·32

Dr. Gladstone has been good enough to measure the refractive power of this substance, and obtained the following results:—

$t°$.	μ_A.	μ_D.	μ_H.	Specific refraction.	Specific dispersion.	Ref. equiv. A.
23°	1·4393	1·4449	1·4611	0·4924	0·0244	90·60

He remarks that "the refraction equivalent of this compound scarcely decides as to the number of carbon-atoms double-linked, but if we suppose only one pair, the theoretical amount would be 89·4, and therefore not much below the experimental, and the specific dispersion strongly supports that view."

Density determinations of this substance gave the following numbers:—

$$d\frac{15°}{15}\ 0·88271,$$

$$d\frac{25°}{25}\ 0·87658.$$

The following are the determinations of its magnetic rotation.

	t.	Sp. rotation.	Mol. rotation.
	24·5°	1·0855	14·589
	25·0	1·0801	14·528
	16·4	1·0857	14·502
	16·4	1·0856	14·501
Average	20·6	1·0842	14·530

If we now compare the molecular rotation of undecylenic acid with that of its ethyl salt, allowing for the change of composition, we get the following result:—

Undecylenic acid, 12·547 + 1·023 × 2 ..	14·570
Ethyl undecylenate....................	14·530
	0·040

This corresponds very closely with the difference found in the case of the fatty series, which is 0·056.

When these substances were examined, it was expected they would give numbers having a series constant (Trans., 1884, 546) of 1·451, the same as that of ethyl α-crotonate and oleate. In that case, the molecular rotation of the ether would have been 14·750 instead of 14·530, which has been found.

On referring to my previous paper (Trans., 1884, 561), it will be seen that two sets of numbers were obtained, when comparing the molecular rotations of unsaturated and saturated compounds. The following is the table given:—

Ethyl α-crotonate..........	7·589	1·112.
,, butyrate............	6·477	
,, oleate..............	21·909	1·112.
,, stearate (calc.)......	20·797	
,, allyl malonate......	11·281	0·914.
,, propyl malonate.....	10·367	
Allyl alcohol..............	4·682	0·914.
Propyl alcohol............	3·768	

From this it is seen that allyl compounds give a smaller difference in relation to the saturated compounds than the α-crotonic and oleic compounds.

Now if the molecular rotations of undecylenic compounds be compared with those of the corresponding saturated compounds, it will be seen that numbers are obtained which differ only to a very slight extent from those of allyl compounds.

Undecylenic acid..........	12·547	0·897.
Undecylic acid............	11·650	
Ethyl undecylenate........	14·530	0·890.
,, undecylate..........	13·640	

These results indicate, therefore, that undecylenic acid is an allyl-derivative. This being so, it was thought desirable to examine some allyl-derivative of the fatty acids, which, if the above be true, should be a homologue of undecylenic acid, and thus a stricter comparison of the rotations could be made. For this purpose, allylacetic acid was chosen, and whilst preparing this, it seemed to be of interest to prepare diallylacetic acid, and examine its rotation also. The following is a brief account of the way in which these compounds were obtained.

Ethyl allylmalonate was first made in the usual manner, and fractioned under reduced pressure, to remove unchanged ethyl malonate and any ethyl diallylmalonate which might have been formed. The ether was saponified with caustic potash and the product evaporated on the water-bath until free from alcohol. The alkaline mass was then dissolved, strongly acidified with hydrochloric acid, and the allylmalonic acid thus set free taken up by repeated treatment with ether free from alcohol. The ethereal solution was shaken with calcium chloride to remove as much water as possible, decanted, and the ether distilled off; the acid was then dried on the water-bath, and purified by crystallisation from benzene, which is a very convenient solvent for this purpose. In this way, it was obtained in fine white needles.

Ethyl diallylmalonate was also prepared in the usual way from

ethyl allylmalonate. Some considerable quantity was made, which was carefully fractioned several times under reduced pressure, and its magnetic rotation and density again determined, as I was not quite satisfied with my previous determinations (Trans., 1884, 539). The boiling point of the product was 207·5—208·5° (corr.) under 260 mm. The density determinations gave—

$$d\frac{6·5°}{6·5}\ 1·00620.$$

$$d\frac{15°}{15}\ 0·99940.$$

$$d\frac{25°}{25}\ 0·99252.$$

These numbers are not very different from those of the specimen previously examined, which were for—

$$d\frac{15°}{15}\ 0·99997, \text{ and for } d\frac{25°}{25}\ 0·99301.$$

The following are the numbers obtained for the magnetic rotation of this new preparation :—

	t.	Sp. rotation.	Mol. rotation.
	13·5°	1·1277	15·030
	13·5	1·1265	15·013
	14·0	1·1274	15·031
Average	13·7	1·1272	15·025

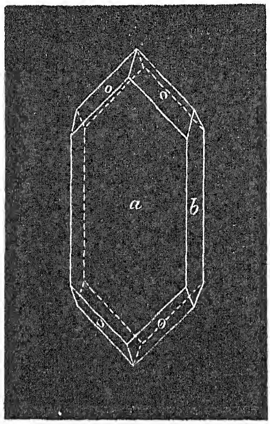
The previous number obtained for the molecular rotation was 14·998, and therefore only differs from this new one by 0·027.

To obtain the diallylmalonic acid, the ether was treated with caustic alkali, and all the alcohol driven off from the alkaline product on the water-bath; it was then dissolved and acidified strongly with hydrochloric acid, when the diallylmalonic acid separated as a magma of fine crystals. After standing for some time, these were collected on a calico filter and well pressed from the saline solution; the latter being treated with ether to recover any acid remaining in solution. The crude acid was crystallised two or three times from water, and in this way was obtained in beautiful large prisms. Professor Haushofer has been good enough to measure these crystals, and gives the following account of them.

"Crystalline system, Rhombic."

Transparent brilliant crystals of the combinations $\infty\bar{P}\infty(100) = a$. $\infty\breve{P}\infty(010) = b$. $P(111) = o$. Usually prismatically developed by

the predominance of the vertical surfaces *a* and *b*. As a rule the surface *a* slightly predominates; frequently, however, both surfaces



are equally developed, and then the crystals have a distinct tetragonal habitus, about which the measurements of the angles afford no evidence, as there is but little difference between the axes *a* and *b*. Cleavage towards *b*, but not well marked. The surfaces *a* and *b* are usually uneven and not adapted for measurement; there is so great variation in the angles that the determination of the crystalline system rests on the optical properties. Occasionally some indication of the primary brachydome and of the base may be observed:—

	Measured.	Calculated.	
$0 : 0\ (111)\ (\bar{1}11)$	= 108° 54′	— —	(Brachydiagonal polar angle.)
$0 : 0\ (111)\ (1\bar{1}1)$	= 108 36	— —	(Macrodiagonal polar angle.)
$0 : 0\ (111)\ (11\bar{1})$	= 110 53	110° 56′	(Basal angle.)

"A plate cut parallel to the base (which is only effected with difficulty owing to the brittleness of the crystal) shows an interference image in convergent polarised light like a uniaxial crystal; but on turning the plate on the vertical axis the dark arms of the cross separate into two hyperbolas.

"It is difficult to decide how the axial planes lie, as that arm of the cross which is parallel to the macrodiagonal is considerably the stronger. I am inclined to believe that the optical axes lie in the plane of the macrodiagonal. No determination of the relative dispersion or of the optical characters of the substance could be made on account of the weakness of the interference image."

The allyl- and diallyl-acetic acids were obtained by heating the corresponding malonic acids—after being thoroughly dried—in a retort with a reflux condenser until carbonic anhydride ceased to be given off. They were then distilled; their formation takes place very rapidly.

Allylacetic acid thus obtained boiled at 185—188° (corr.), the small variation in its boiling point being probably due to the presence of a minute quantity of the diallyl acid. It has a sharp, acid odour, not unlike that of valeric acid, but with a slight train oil character. It does not solidify when cooled in ice and hydrochloric acid. It floats on water as an oil, but is soluble to some extent in this fluid.

The density determinations gave the following results:—

$$d\frac{12^\circ}{12}\ 0{\cdot}98656.$$

$$d\frac{15^\circ}{15}\ 0{\cdot}98416.$$

$$d\frac{25^\circ}{25}\ 0{\cdot}97670.$$

The following numbers were obtained for its magnetic rotation:—

	t.	Sp. rotation.	Mol. rotation.
	12·5°	1·1429	6·439
	12·5	1·1403	6·424
	14·0	1·1369	6·413
	14·0	1·1380	6·419
	14·6	1·1398	6·432
	14·6	1·1389	6·427
	14·6	1·1403	6·435
	14·6	1·1382	6·425
Average	13·9	1·1394	6·426

The diallylacetic acid obtained as above boiled at 227—227·5° (corr.). It has an odour similar to that of train oil, but somewhat sharper. When cooled with ice and hydrochloric acid, it thickens, but does not solidify: it is only slightly soluble in water. Determinations of its density gave the following numbers:—

$$d\frac{12^\circ}{12}\ 0{\cdot}95756,$$

$$d\frac{15^\circ}{15}\ 0{\cdot}95547,$$

$$d\frac{25^\circ}{25}\ 0{\cdot}94913.$$

The measurements obtained for its magnetic rotation were as follows:—

	t.	Sp. rotation.	Mol. rotation.
	18·5°	1·2681	10·346
	18·5	1·2682	10·347
	18·5	1·2694	10·357
	18·5	1·2692	10·356
	13·0	1·2708	10·329
	13·5	1·2720	10·343
	14·0	1·2699	10·329
Average	16·4	1·2697	10·344

If from the molecular rotation obtained for allylacetic acid we subtract that of the corresponding saturated compound, valeric acid, we get the difference due to the influence of the allyl-group—

Allylacetic acid	6·426
Valeric acid	5·508
	0·918

If we do the same with diallylacetic acid, and subtract from it the molecular rotation of octylic acid, we get—

Diallylacetic acid....................	10·344
Octylic acid	8·577
	1·767

This number is the difference due to the influence of two allyl-groups, but it will be seen that it is less than twice that of the first replacement; if we subtract the one from the other we get—

Two allyl-groups	1·767
1st allyl-group	0·918
2nd " "	0·849

This is quite consistent with previous observations on successive replacements of all kinds. In the case of ethyl diallylmalonate, the influence of this second replacement cannot be found because ethyl dipropylmalonate has not yet been examined, and the malonic series has not been sufficiently studied to calculate this. There is very little doubt, however, that it is nearly the same as in the above, and if so we then find that ethyl dipropylmalonate should have a rotation of about 13·246, which is very probable judging from other results.

In reference to undecylenic acid, however, the interest attaches to

monallyl compounds. In my previous experiments, I found that the difference between an allyl and a saturated compound was 0·914. This is further confirmed by the examination of allylacetic acid, which gives 0·918, a number a little higher, but the difference is so very small that the two may be regarded as identical. This result therefore strengthens the inference that undecylenic acid is an allyl fatty acid. Still the numbers which are already given in this paper for this substance and its ethyl salt being part of some of the earlier work on the magnetic rotation, to which a small correction, since discovered, should have been applied, it was thought desirable to re-measure either the acid or the ethyl salt; the latter was selected as being the purer product, and, being liquid at the ordinary temperature, is more convenient for examination. The new results were as follows:—

	t.	Sp. rotation.	Mol. rotation.
	13·6°	1·0898	14·528
	13·4	1·0894	14·554
	13·8	1·0910	14·526
	13·8	1·0908	14·543
	14·6	1·0917	14·564
Average	13·6	1·0905	14·543

Now if from this molecular rotation we subtract that of ethyl undecylate we get—

Ethyl undecylenate............	14·543
„ undecylate..............	13·640
	0·903

and it will be seen that this difference is nearly identical with that of the allyl compounds, being only 0·011 less, which, considering the high molecular weight of the substance and comparatively low specific rotation, is as close as could be expected.

From the foregoing results, it is seen that undecylenic acid and its ethyl salt give magnetic rotations which are peculiar to monallyl-derivatives of the fatty acid and other series, being lower than any other unsaturated compounds yet examined. This remark refers to the bibasic acids, citraconic, itaconic, and maleïc, as well as those given in my previous paper, and thus indicates that the acid in question is an allyl-derivative of a fatty acid. If this be so, and there is no reason for doubting it so far as can be seen, the next question is as to what is the position of the allyl-group, whether this acid be, for example, an allyl-hexyl-acetic acid or an allyl-octylic acid—

$$\begin{matrix} C_3H_5 \\ C_6H_{13} \end{matrix}\!\!>\!CH{\cdot}COOH, \text{ or } C_3H_5{\cdot}C_7H_{14}{\cdot}COOH.$$

The answer to this is given by the oxidation product it yields when treated with nitric acid. Krafft has shown that under these circumstances it yields sebacic acid; now for this to be formed it must be an allyloctylic acid, which may be written thus:—

$$CH_2 : CH{\cdot}CH_2{\cdot}(CH_2)_7{\cdot}COOH.$$

The oxidation would remove the CH_2 and convert the CH next to it into COOH, yielding

$$COOH{\cdot}(CH_2)_8{\cdot}COOH,$$

in the same way as its homologue, allylacetic acid, under similar circumstances, gives succinic acid.

There is one reaction of undecylenic acid which is very remarkable, and that is, that when it is fused with caustic alkali it yields nonylic acid; this reaction is difficult to explain unless sebacic acid is first formed and then gives up carbonic anhydride, thus:—

$$COOH{\cdot}(CH_2)_8{\cdot}COOH = CH_3{\cdot}(CH_2)_7{\cdot}COOH + CO_2,$$

but, judging from small experiments made in this direction, this does not seem to be the case.

If undecylenic acid had the constitution

$$CH_3{\cdot}(CH_2)_7{\cdot}CH : CH{\cdot}COOH,$$

the formation of nonylic acid under those circumstances would be in accordance with experience, but this cannot be the case, otherwise it would have a much higher molecular rotation, and moreover it would not yield sebacic acid on oxidation with nitric acid. It therefore appears that undecylenic acid is allyloctylic acid or, which is the same thing, vinylnonylic acid,

$$CH_2 : CH{\cdot}(CH_2)_8{\cdot}COOH.$$

I hope shortly to bring before the Society an account of the magnetic rotations of the unsaturated bibasic acids and their so-called physical isomerides.

XXIV.—*On the Condition of Silicon in Pig Iron.*

By A. E. JORDAN (Student in the Chemical Laboratories, Mason College, Birmingham) and THOMAS TURNER.

SILICON, like carbon, is stated to exist in three forms, the amorphous variety corresponding to charcoal, the graphitic to graphite, and the adamantine to the diamond. Amorphous silicon is distinguished by its solubility in hydrofluoric acid. The chemical properties of graphitic and adamantine silicon are said to be the same, both varieties being insoluble in hydrofluoric acid, and unaffected by heating in oxygen, though soluble in a mixture of nitric and hydrofluoric acids. The graphitic variety forms thin hexagonal plates, while the adamantine modification crystallises in octahedra. It has been affirmed by Professor W. H. Miller that the plates of so-called graphitic silicon are modifications of the octahedral form, and it is therefore probable that only two really distinct varieties are known.

As silicon is a constant constituent of pig iron, and as it may readily be obtained in a crystalline form by separation from solution in various metals, it seems natural to expect that silicon, like carbon, would separate from cast iron in the graphitic condition. It is generally so stated in metallurgical books, and a number of workers have at various times confirmed this view.

Thus Mr. J. A. Phillips ("Metallurgy," p. 115) says, "Cast iron often contains silicon in the graphitic state," while Dr. Percy, speaking of the insoluble residue left by the action of diluted acids on grey cast iron, says ("Iron and Steel," p. 145), "There is reason to believe that crystallised silicon may also not unfrequently be present," and adds, "Mr. T. H. Henry informed me that he found crystallised silicon amongst the graphitic scales obtained by the action of hydrochloric acid on pig iron." In Wagner's *Jahresbericht* (1857, iii, 8) a reference is given to some analyses by Wöhler, who is stated to have found crystallised silicon in cast iron. Professor Robert Richter, of Leoben, also observed crystallised silicon in cast iron (*Berg und Huttenman, Jahrbuch*, 1862, 289). A specimen of finely crystallised cast iron was extracted with dilute hydrochloric acid so long as anything dissolved, the residue was washed, dried, and ignited in a stream of oxygen. It was then extracted with hydrochloric acid to remove oxide of iron, washed, and dried. It now contained thin graphitic-looking plates, with a metallic lustre, which were not affected by further heating in oxygen. These plates were readily oxidised when heated with potassium nitrate and sodium carbonate,

yielding some oxide of iron and silica. Richter concluded from this that these plates were identical with Deville's crystallised silicon, then newly prepared, and appears to have regarded the oxide of iron merely as an accidental impurity.

An important paper was read by Mr. Snelus at the Merthyr meeting of the Iron and Steel Institute, 1870, and was afterwards published in the first volume of the Proceedings of the Institute (p. 28). In this paper, conclusions were arrived at which are entirely different from those previously mentioned. Thus, while Snelus was able by means of a magnet, or by careful sifting, to more or less completely separate graphitic carbon from cast iron, he was unable in this way to separate silicon. On the contrary, the proportion of silicon present in the iron was actually increased, probably owing to the separation of carbon by the methods employed; and after a number of careful experiments on pig iron containing a considerable proportion of silicon, Snelus concluded that silicon "must have been in solution or combination in the iron, and that it is at least an exceptional case if it is found in the free state" (p. 35).

The question was attacked in an entirely different manner by Mr. Morton (*Chem. News*, **29**, 107), who showed that the silicon in a silicious pig iron (4·6 per cent. Si) was wholly converted into silica by heating it in sealed tubes, either with Nordhausen sulphuric acid or with iodine, in an atmosphere of carbon dioxide; and although graphitoidal silicon was sought for it was not found in these experiments.

Some interesting observations have also been made by Dr. Tilden (*Proceedings Birmingham Philosophical Society*, **3**, 203), who, when examining a silicious Staffordshire pig iron, obtained a quantity of black scales in the residue after treatment with dilute hydrochloric acid which did not burn when heated in a muffle, but which were proved to contain iron, and from which amorphous silicon was separated, as a brown powder, by protracted boiling with hydrochloric acid. Dr. Tilden suggested that by prolonged boiling, the residue might have been caused to yield up the whole of its iron, and that possibly in those cases where graphitic silicon was supposed to have been observed, the substance was in reality a silicide of iron or manganese, resembling the compound described.

Our own experiments were of three kinds, including—

1. A magnetic examination of certain specimens which appeared most likely to contain crystallised silicon.

2. An examination of the residue left on prolonged treatment with dilute hydrochloric acid.

3 Some experiments on graphitic matter separated from cast iron.

Magnetic Examination.

Five specimens of cast iron were operated upon in this manner, but as the results in each case are similar, so far as the absence of graphitic silicon is concerned, it will perhaps be sufficient if we describe the experiment which we consider most conclusive.

35 grams of silicon pig, containing 9·8 per cent. of silicon, was taken after crushing and passing through a 60 sieve. It was laid upon a clean piece of paper, and then everything attracted by means of a magnet was removed on to a similar sheet of paper, by drawing the magnet repeatedly through the mass. This was again and again repeated so long as any perceptible residue was left. These residues were mixed together and further treated by the magnet, and at length a small residue was obtained which appeared to be quite indifferent to magnetic influence. The weight of this residue was 0·11 gram, or 0·32 per cent. of the original material. When examined under the lens, it was seen to contain some black graphitic particles, which entirely burned off on afterwards heating in the muffle, and were evidently graphitic carbon. Some slightly coloured, sometimes angular, and at other times rounded fragments were present; they appeared to be nearly transparent, and were probably sand, either accidentally introduced or perhaps mechanically intermixed during the running of the pig. The greater part of the residue which did not burn off in the muffle, however, was nearly white, quite opaque, and generally in rounded nodules; this was evidently slag, of which a similar specimen of iron has already been shown to contain 0·76 per cent. (Turner, Trans., **45**, 265). Now since the graphite in this iron is only present to the extent of about 1 per cent., and slag to an even smaller extent, it is scarcely conceivable that graphitic silicon could exist in any quantity in the iron without being separated, at least to some extent, along with the graphite and slaggy matter. And, certainly, if graphitic silicon does occur in cast iron at all, silicon pig would appear to be the most probable material in which it should be found.

Examination of Insoluble Residues.

For these experiments, five specimens of iron were examined, in which the proportions of silicon and graphitic carbon varied considerably. The method adopted in their examination was proposed to us by Dr. Tilden, to whom we are indebted for several suggestions in connection with this part of the work.

1. *South Staffordshire White Iron.*—The metal was crushed in a steel mortar, and passed through a sieve; 40 grams was taken and boiled repeatedly with dilute hydrochloric acid (about 1 of strong

acid with from 2 to 3 of water) until no more iron was extracted, as indicated by testing the solution with potassium ferrocyanide. After being thoroughly washed with hot water, the residue was dried and heated in a muffle, the temperature of which was at about the point necessary for the cupellation of silver. The residue burned quite white, and was entirely soluble in hydrofluoric acid, and could therefore have contained no graphitic silicon. In order to be certain that heating in the muffle was not capable of oxidising graphitic silicon, we placed a specimen of the pure substance in the muffle under exactly the same circumstances as the residues to be examined, and after a lengthened exposure the specimen of graphitic silicon was apparently unaltered.

2. *No.* 3. *Hematite Pig.*—This iron contained 2·6 per cent. of silicon, and was used in the form of borings, 40 grams of which was taken for the experiment. It was repeatedly extracted with dilute hydrochloric acid as before, the residue thoroughly washed, dried, and ignited in the muffle. The residue was quite white, and entirely dissolved in hydrofluoric acid. It could therefore have contained no crystallised silicon.

3. *No.* 2. *South Staffordshire Grey Iron.*—In this case, 40 grams was heated with hydrochloric acid, &c., exactly as before. But on burning off the carbon a residue was left, slightly brown in colour, and on extraction with hydrofluoric acid a brown residue remained. It was very small in quantity, and resembled oxide of iron in appearance. Though insoluble in hydrochloric acid, it yielded a portion of iron when evaporated with hydrofluoric and hydrochloric acids alternately. When dried and examined under the microscope, nothing resembling graphite was observed in the residue, which was probably silicide of iron partly oxidised by roasting in the muffle.

4. *No.* 1. *Middlesbrough Grey Pig* (*Clarence Works*).—In this case, the same quantity was taken as before, the methods adopted being also similar. The results obtained exactly resembled those of the first two specimens.

5. *Govan Silicon Pig.*—This specimen contained 10·3 per cent. of silicon. It was crushed in a steel mortar, and sieved to ensure uniformity in size of the fragments, 40 grams being taken for the experiment. This was boiled repeatedly for many hours with dilute hydrochloric acid, until no more iron was dissolved by the liquid. The residue, after washing and drying at 100°, was of considerable quantity and grey in colour. A portion of this was roasted in the muffle, when a slightly brown residue was left. On extracting this with hydrofluoric acid, brilliant scales were left which much resembled graphitic silicon in appearance; but on roasting these scales for a considerable time in the muffle they gradually lost their lustre,

becoming dark brown and much like oxide of iron in aspect. This residue was quite insoluble in hydrochloric acid even on boiling, but on evaporating repeatedly with hydrofluoric acid it then yielded a small quantity of iron when again extracted with hydrochloric acid. This brown substance was, however, soluble when heated for some time with hydrochloric acid in a sealed tube at 140°, and on qualitative examination proved to contain titanium in small quantity. There is no doubt, therefore, that the scales which remained, after roasting and extraction with hydrofluoric acid, consisted almost entirely of difficultly decomposable silicide of iron, while no crystallised silicon was present. It will be remembered that in Richter's experiments, previously mentioned, a small quantity of oxide of iron was obtained from the graphitic scales, in addition to silica. They may therefore very possibly have resembled those obtained in our own experiments.

A portion of the residue, before roasting, and after drying at 100°, was next examined. It was mixed with a little solid potash in a tube, and arrangements made for collecting any gas which might be evolved. On melting the potash by applying a gentle heat, a violent action ensued and some hydrogen was evolved. This has been considered by some writers an evidence of the existence of free silicon; but it has been stated by Allen (*Chem. News*, **29**, 91; **40**, 65) that the solution of silicious pig iron in dilute hydrochloric or sulphuric acid gives rise to the production of Buff and Wöhler's "leucone" (*Watts' Dict.*, **5**, 274, Miller, Part II, p. 280, 1878), and this is probably the correct explanation of the action. Leucone, according to Wöhler, has the formula $3SiO,2H_2O$, and may be regarded as a hydrate of the monoxide of silicon; but Friedel and Ladenburg regard it as silicon formanhydride ($Si_2H_2O_3$). The residue to which we have referred dissolved readily in weak warm hydrofluoric acid, evolving hydrogen with effervescence; it also decolorised acidified solution of potassium permanganate; and when strongly heated in a test-tube, partly closed at the top by the finger, a slight explosion took place, caused by the evolved hydrogen. In these characters, as well as in its permanency at 100°, and the evolution of hydrogen with potash, it exactly resembles leucone. It is probable, however, that only a small portion of the residue consisted of this substance, as it is readily oxidised in the presence of ferric salts, and hence would be gradually destroyed in the process of solution. But the fact of its formation negatives any evidence in favour of the existence of crystalline silicon in cast iron, founded upon the evolution of hydrogen on treatment of these residues with molten potash. It will be remembered we have previously shown that this residue does not contain graphitic silicon, though it does contain scales which resemble that substance.

In the foregoing experiments on residues from cast iron, we have examined specimens which were intended to be as far as possible representative, and in no case have we met with any evidence of the existence of crystalline silicon. We have, however, observed facts closely resembling those adduced in support of its occurrence in cast iron, and which may help in some measure to account for mistakes in the case of some earlier observers. For it must be remembered that about 25 years ago, when the work of Deville and Wöhler was being performed or was quite new, crystalline silicon was often supposed to have been observed, while now, when analyses are much more frequent, its occurrence is seldom or never recorded.

Examination of Graphite.

Since the amount of graphitic carbon is generally greatest when carbon and silicon are present in nearly equal proportions, it appeared probable that graphitic matter separated from cast iron would contain crystallised silicon, if it ever separated from cast iron in this condition. We therefore examined two very fine specimens, one of graphite and the other of kish, for both of which we are indebted to the kindness of Dr. Percy.

1. *Graphite from Dowlais.*—This specimen was forwarded to Dr. Percy from Mr. Child, of Dowlais, one of his former pupils. It was examined by Dr. Percy, and is mentioned in his "Iron and Steel," p. 145. After being digested with hydrochloric acid, it was washed, dried, and put into molten potash in a gold crucible. "Much effervescence took place, due to the evolution of gas, which ignited at the surface just like hydrogen. When native graphite was similarly treated there was not the slightest effervescence." Dr. Percy regarded this action as probably caused by free silicon.

In talking of this experiment a short time since with one of us, Dr. Percy in the kindest manner offered to place the whole of this specimen which he had left in his collection at our disposal if necessary, so that the correctness of the above inference might be ascertained. For this purpose, a quantity was taken and digested with strong hydrochloric acid, and afterwards with a 5 per cent. solution of potash, neither of which reagents appeared to be capable of extracting anything from the specimen. It was then dried and heated in the muffle. Part burned off very rapidly, while another portion required much longer for its combustion, but ultimately only a very small brown ash remained. This dissolved in boiling hydrochloric acid, leaving only two or three minute white specks, while the solution contained a small quantity of iron. The specimen would appear, therefore, to be almost entirely free from silicon in any form, and to be remark-

ably pure graphitic carbon. It is quite conceivable from the known variations in the igniting point of different varieties of carbon, that a portion of this pure form of graphite might evolve a combustible gas in contact with fused potash, while the less combustible part and native graphite would remain entirely unaffected at the temperature employed. This is probably the explanation of the effect observed by Dr. Percy.

2. *Kish from Middlesbrough.*—For this fine specimen, we are also indebted to Dr. Percy. It was part of a larger quantity forwarded to him from Clarence Works. It was repeatedly extracted with hydrochloric acid, which removed a considerable quantity of iron and also some manganese. The residue was extracted with 5 per cent. solution of potash and some silica removed. There were left behind some fine plates of graphite, and what was probably a few grains of sand with which the kish had been contaminated. On drying and burning in the muffle, the residue was light brown, but became quite white on prolonged digestion with hydrochloric acid. This specimen was therefore free from crystallised silicon.

In addition to the facts already considered, there is an argument in support of the existence of crystallised silicon in cast iron, which was mentioned by Sir I. Lowthian Bell in the discussion which followed the paper by Mr. Snelus, to which previous reference has been made. Under certain circumstances, pig iron is observed to be covered with a peculiar soft downy coating on its upper surface, resembling wool in appearance, but consisting of silica. It has been suggested that this is produced by the oxidation of silicon exuded by the iron in solidification, and that probably this variety of iron contains graphitic silicon. But such an argument can by no means be taken as proof of the fact; and we may so far anticipate a future communication as to state that an exactly similar covering of silica has been observed by one of us, in a case where the most careful examination failed to yield any evidence of the presence of graphitic silicon.

We are aware that a considerable accumulation of negative evidence is necessary before it can be considered absolutely conclusive. At the same time we feel that in this matter a tolerably strong case has been made out. Thus, while it is not possible to separate silicon from iron either by sifting or by a magnet, and it cannot be detected in the residue left by the action of a diluted acid or in graphitic matter, it has been obtained in the amorphous form by Dr. Tilden from scaly silicide of iron. It is probable, therefore, that silicon exists in cast iron in the form of a silicide (or silicides) which is dissolved when fluid in the excess of iron present. The silicide itself is attacked by acids only with considerable difficulty, but when present in small quantity, being more finely divided, it is easily decomposed. On the

other hand, evidence in favour of the existence of crystallised silicon in cast iron is at present very unsatisfactory, and would require to be considerably strengthened before it could be accepted.

XXV.—*Reactions supposed to yield Nitroxyl or Nitryl Chloride.*

By W. COLLINGWOOD WILLIAMS, B.Sc., Tangye Scholar in the Mason Science College, Birmingham.

IN all the larger text-books that I have examined, it is stated that nitryl chloride not only exists, but is readily prepared.

These statements are based on the researches of Odet and Vignon (*Compt. rend.*, **69**, 1142, and **70**, 96), Williamson (*Proc. Roy. Soc.*, **7**, 15), and Hasenbach (*J. pr. Chem.* [2], **4**, 1).

When these papers are examined, however, it is at once obvious that the definite and plausible statements of the text-books are based on very imperfect evidence. Odet and Vignon, in the papers cited, were working in the hope of elucidating the process introduced by Deville for the preparation of nitrogen pentoxide. The formation of the latter by the action of chlorine on silver nitrate, they explain by the equations—

$$\left.\begin{matrix}NO_2\\Ag\end{matrix}\right\}O + Cl_2 = AgCl + NO_2Cl + O \;\ldots\ldots\ldots (1),$$

$$\left.\begin{matrix}NO_2\\Ag\end{matrix}\right\}O + NO_2Cl = \left.\begin{matrix}NO_2\\NO_2\end{matrix}\right\}O + AgCl \;\ldots\ldots\ldots (2),$$

and in order to test the correctness of these equations, they resolved to bring nitroxyl chloride into contact with nitrate of silver.

It is therefore with some surprise that one learns that in order to prepare the nitroxyl chloride they have recourse to a reaction in which, if formed, it will on their own hypothesis be immediately decomposed, viz., the action of phosphorus oxychloride on excess of lead or silver nitrate. It is stated that the product boiled at 5°, and it is described as of a pale-yellow colour.

In their second investigation, in which they endeavoured to obtain the nitroxyl chloride formed as an intermediate product (according to their view) in Deville's process, they say that they were five hours in collecting 2 c.c. of liquid, which they assume to be nitroxyl chloride. It boiled in the hand, and was yellowish-brown in colour.

In neither paper is there any account of a quantitative examination, nor did they take any steps to identify the compound.

Thus far Odet and Vignon. Turning to Williamson's paper (*loc. cit.*), we find that he poured sulphuryl chlorhydrin, $SO_2Cl{\cdot}OH$, on dry fused nitre, and found that a gas smelling of aqua regia was evolved, giving hydrochloric and nitric acids when passed into cold water. This, he remarks, is doubtless nitryl chloride.

Hasenbach passed a mixture of chlorine (in excess) and nitric peroxide through a *strongly heated combustion-tube*. Since no temperature is stated, I think one is justified in supposing that the tube was red-hot. As to the product, he merely says that it was "possessed of the properties of NO_2Cl." After one rectification the liquid was considered pure and contained 44 per cent. of chlorine, the theoretical quantity for NO_2Cl being 43·5 per cent.

This coincidence I regard as purely accidental; for in the first place, the analysis of only one specimen is given, and secondly, in my own experiments, when working under like conditions, I have never obtained a liquid with even approximately a constant boiling point, or which could be considered pure after one redistillation.

The large *proportion* of chlorine is readily accounted for by the fact, as I shall show, that nitrosyl chloride, NOCl (54 per cent. Cl), is a principal product, and further, that chlorine dissolves to a large extent both in NOCl and in N_2O_4.

It is also worthy of remark that in endeavouring to prepare NO_2Br by the direct union of NO_2 and Br, Hasenbach found only 34 per cent. Br in the product, as against 63 per cent. theory. NO_2I could not be prepared.

On the other hand, Armstrong in 1873 found that when acetic chloride acts on a nitrate, the *components* of nitryl chloride are formed, but not the substance itself. Peroxide of nitrogen and chlorine are evolved, while a certain quantity of acetic anhydride is produced simultaneously (*Chem. Soc. J.*, 1873, **26**, 683).

From *nitrites* on the contrary, nitrosyl chloride was readily obtained by similar treatment.

Quite recently, however, reactions of the same class have been re-examined by Lachowicz (*Ber.*, **17**, 1281; **18**, 2990). He does not seem to be aware of Armstrong's experiments, for he makes no mention of them, and states that from silver nitrate and an acid chloranhydride, the acid anhydride is obtained. By this reaction, he prepared acetic, benzoic, and phthalic anhydrides in theoretical quantity. The gaseous products are peroxide of nitrogen and *oxygen*. Here he differs both from Armstrong and myself, but in any case the reaction does not avail for the preparation of nitryl chloride. Lachowicz gives as the typical equation for this decomposition, $2AgNO_3 + 2X{\cdot}COCl = 2AgCl + [X{\cdot}CO{\cdot}]_2O + N_2O_4 + O$, where X is a hydrocarbon radicle.

Judging, therefore, by the light of previous research, it appears that the evidence for the existence of nitryl chloride is by no meams complete.

With the object of further investigating this question, and of preparing nitryl chloride for use as a reagent, I have made a number of experiments such as might be expected to yield the substance. I shall now proceed to describe these.

1. *Action of Phosphorus Oxychloride on Lead Nitrate in Excess.*

This reaction was discussed some time ago by Mills (*Phil. Mag.* [4], **40**, 134). Oxychloride of phosphorus contained in a tap funnel was allowed to drop on to pure dry lead nitrate in a distilling flask, connected with a spiral condenser cooled by a freezing mixture of ice and salt, the flask being surrounded by warm water to promote reaction.

This process fails utterly as a source of nitryl chloride. No liquid product was obtained in any quantity, and throughout the experiment a gas having the smell and bleaching properties of chlorine escaped. The vapours in the flask had a reddish colour, resembling that of dilute nitrogen peroxide, and after the experiment had gone on for some hours, a few drops of a yellowish-red liquid were collected, but the quantity was far too small to be of any use.

2. *Action of pure Nitric Acid on Phosphorus Oxychloride in Excess.*

The same apparatus was used, the $POCl_3$ being now placed in the flask. The reaction seemed at first more promising than the last, as more liquid distillate was obtained. On examination, however, it was found that all distillates contained $POCl_3$, even though distilled at 20° to 30°, and it therefore seemed likely that the nitryl chloride, if formed in this way, combined with the excess of $POCl_3$.

3. *Action of Nitric Acid on Phosphorus Oxychloride in Equivalent Proportions.*

The materials were heated at 100° for about two hours in sealed tubes. The contents separated into two layers, the upper deep red and mobile, the lower yellow and viscid. The latter consisted doubtless of phosphoric acid. On opening the tubes, a very volatile vapour having the odour of aqua regia escaped, which did not condense at $-19°$. A portion of this vapour was collected over strong sulphuric acid, and after absorption of the hydrochloric acid gas by water, was found to be chlorine.

It is probable that through dehydration of the orthophosphoric

acid, and consequent formation of hydrochloric acid, the aqua regia reaction took place, with production of chlorine and nitrosyl chloride. On account of this complication, the reaction was not further studied, but, after the experiments of Williamson with sulphuryl chlorhydrin had been repeated, it was decided to use sulphuryl dichloride and nitric acid, or potassium nitrate, in which case dehydration of the resulting acid was not probable. I should mention that the reaction between nitric acid and phosphorus oxychloride takes place, to all appearance completely, in the cold after long standing. In this respect, the action of phosphorus oxychloride is in marked contrast with that of sulphuryl dichloride.

4. *Action of Sulphuric Chlorhydrin,* $SO_2(OH)Cl$, *on Potassium Nitrate in Equivalent Proportions.*

When a small quantity of the dry fused nitrate is placed in a test-tube and sulphuric chlorhydrin is added to it, the mixture becomes hot and evolves chlorine. Subsequently, on applying heat, nitric peroxide is given off in large quantity. No other substance save these two could be detected, even when considerable quantities of the materials were employed in equivalent proportions, and the evolved vapours passed through a condenser cooled to $-18°$. At first, chlorine alone escaped and no liquid condensed, but on the application of heat to the flask red vapours were formed, which on passing into the condenser gave a small quantity of a deep red liquid now perfectly familiar to me as a solution of chlorine in nitrogen peroxide. The issuing gas on being passed into *hot* water always gave *chlorine*. With *cold* water, of course hydrochloric acid is produced, due to the oxidation by the chlorine of the nitrous acid formed by the solution of the peroxide in water.

The "gas smelling of aqua regia" is therefore chlorine together with a little nitrogen peroxide, and it is noteworthy that the evolution of the chlorine *before* the peroxide was also observed by Armstrong when potassium nitrate is treated with acetic chloride.

Possibly the nitric peroxide first formed combines with unattacked chlorhydrin, forming a nitrosyl compound, in this way :—

$$\text{(i.)}\ 2SO_2(OH)Cl + 2KO{\cdot}NO_2 = 2SO_2(OH)(OK) + N_2O_4 + Cl_2,$$
$$\text{(ii.)}\ SO_2(OH)Cl + NO{\cdot}NO_3 = SO_2(O{\cdot}NO)Cl + HNO_3,$$

while the chlorine escapes. When heated, such a compound might easily decompose in presence of excess of potassium nitrate, forming chlorine and nitric peroxide, the latter being now in excess :—

$$\text{(iii.)}\ 2SO_2(O{\cdot}NO)Cl + 4NO_2{\cdot}OK = 3N_2O_4 + Cl_2 + 2SO_2(OK)_2.$$

5. *Action of Sulphuryl Dichloride*, SO_2Cl_2, *on Potassium Nitrate.*

This experiment was tried as a crucial test of this class of reaction. Sulphuryl dichloride was prepared by heating the chlorhydrin in sealed tubes for some days at 180°, the liquid being then distilled on a water-bath. The product, which contained 98 per cent. SO_2Cl_2, was sealed up in a tube with an equivalent quantity of potassium nitrate (*upon which it could not be made to act in an open tube*), and heated at 100° for some hours. A certain amount of red gas was formed, and on opening the tube chlorine was collected over hot water. This does not leave much room for doubt that the reaction is—

$$SO_2Cl_2 + 2KO{\cdot}NO_2 = N_2O_4 + Cl_2 + SO_2(OK)_2.$$

The reaction takes place with great difficulty, and is very incomplete.

Towards absolute nitric acid, sulphuryl dichloride exhibited still greater inertness.

From such experiments as I have described, I infer that generally when a nitrate is acted on by an acid chloride—conditions under which we might reasonably expect nitroxyl chloride to be formed—we do not obtain this substance, but, instead of it, its component parts, nitrogen peroxide and chlorine.

6. *Action of Chlorine on Nitric Peroxide.*

I now pass to the consideration of the method of direct union suggested by Hasenbach.

Three principal series of experiments were performed under this head: in the first, which I shall call series A, the chlorine and peroxide of nitrogen were passed through a *red-hot tube*, in the other two, the components were heated at a temperature not exceeding 150°. The difference between series B and C will be explained later.

A. In these experiments, the chlorine, generated from manganese dioxide (in lumps) and hydrochloric acid, washed with water, and dried by sulphuric acid, was bubbled through liquid peroxide of nitrogen, contained in a wide test-tube which could be warmed if necessary. The vapours were thoroughly mixed in a dry Woulff's bottle and then entered the combustion tube, which was packed with small pieces of clay pipe and heated to redness. Condensation was effected in a spiral condenser cooled by ice and salt, the receiver, a small Würtz flask, being also well cooled in a similar way. The uncondensed gas passed away by the delivery tube of the latter. A closed receiver of this kind was found to be absolutely necessary, as many

experiments failed owing to the rapid action of the moisture of the air on the product.

Now, since NO_2 dissociates at a red heat into NO and oxygen, it was likely that NOCl would be a chief product. *A portion of the escaping gas, on being tested, was found to contain a large proportion of oxygen*, thus proving indirectly the presence of *nitrosyl chloride*. The product was a very volatile, mobile, crimson liquid, and in order to ascertain its composition a portion was distilled through a series of large thin glass bulbs, previously weighed. When about full, the bulbs were sealed, temperature and pressure being noted, and weighed again.

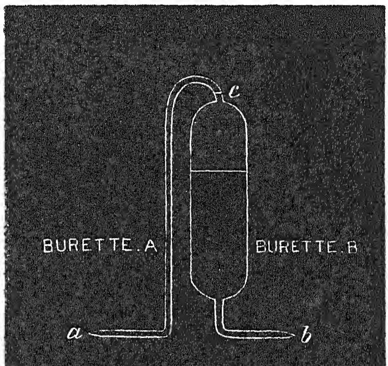


FIG. 1.

The contained vapour was now absorbed by water, a process accomplished by connecting the two extremities *a* and *b* of the bulb with burettes A and B, filled with water, the intervening tubing being also quite full. The point *a* was then broken off inside the tube, and the vapour was rapidly absorbed. When absorption was complete the point *b* was broken, and a little more water sucked over to wash out the tube *a*.

Burette A was now completely filled and inverted in a beaker of water, and the levels being adjusted, a mark was made at *c* where the water stood in the narrow tube. Burette B was now read, and from it water was run into the bulb (through *b*) till its level rose to the mark *c*, when B was again read. This gave the volume of unabsorbed gas, the greater part of which was now contained in the burette A. The contents of the bulb were then washed into a beaker for the determination of the chlorine. The volume of gas in A was read and the nitric oxide then absorbed by ferrous sulphate solution, after which the volume of

residual gas (nitrogen) was again read. From these readings, it was known how much nitrogen and, consequently, how much air had been unexpelled from the bulb during distillation; this volume was subtracted from the total capacity of the bulb, which was now measured by running in water from a burette.

The data thus obtained furnished material for the determination of the vapour-density and of the chlorine present in the gas. The following table contains the numbers. Of the bulbs, No. I is nearest the distilling flask, and contains therefore the least volatile portion of the vapours.

SERIES A.—*Bulbs sealed at* 18·5° *and* 728·8 *mm.*

	I.	II.	III.
V_b	118·6	155·2	176
V_a	0·85	1·0	1·4
V_v	117·75	154·2	174·6
B_v	18·1513	4·5168	23·8571
B_a	17·9341	4·2374	23·5376
W_{v-a}	0·2172	0·2794	0·3195
W_a	0·1367	0·17906	0·20275
W_v	0·3539	0·45846	0·52225
AgCl	0·3076	0·4077	0·4794
V.D.	37·35	36·95	37·17
Cl per cent..	21·5	22·00	22·71

V_b = vol. of bulb; V_a = vol. of unabsorbed air; V_v = vol. vapour;
B_v = weight of bulb full of vapour; B_a = weight of bulb full of air;
W_{v-a} = weight of vapour − weight of equal vol. of air;
W_a = weight of equal vol. of air (calc.); W_v = weight of vapour.

In order to interpret these results, the following assumptions and calculations were made.

Hypothesis α.—If we assume that all the chlorine is combined as NOCl, the volume of the latter can be calculated from the percentage of chlorine, and hence the partial pressure on the admixed peroxide. Then by means of the formula and tables of Professor J. W. Gibbs (*Chem. News*, 1879, 298) the extent of the dissociation of the peroxide can be determined. From this, the percentage composition of the gas in the bulb is known, and the density of this mixture is then readily obtained by a very simple calculation.

Hypothesis β.—The chlorine is supposed to be free, and the calculation made in the same way.

Hypothesis γ.—Nitroxyl chloride is supposed to be the chlorinated substance.

The calculated and observed numbers are contained in the following table, but the figures for the density of the gas in the first bulb obtained on hypotheses β and γ, were so wide of the mark that it was thought unnecessary to work out the results for bulbs II and III:—

SERIES A.

	I.		II.		III.	
	Densities.	Diff.	Densities.	Diff.	Densities.	Diff.
Found..........	37·35	—	36·95	—	37·17	—
Calc. α	37·88	0·53	38·08	1·13	37·92	0·75
„ β	40·92	3·57	—	—	—	—
„ γ	41·00	3·65	—	—	—	—

There can be little doubt therefore that when chlorine and nitric peroxide are passed through a red-hot tube the product is a mixture of nitric peroxide with nitrosyl chloride, although no doubt some chlorine is present in both in solution.

B. In these experiments, the mixed gases, obtained as before, were led through a large U-tube filled with broken glass and heated in an air-bath to a temperature varying from 130° to 150°. This temperature was chosen as being about that at which nitric peroxide completely dissociates into $2NO_2$, and at which therefore one would naturally suppose that direct combination with chlorine would most readily take place.

The product of the experiment was a red volatile liquid similar to that obtained in series A, but since *no oxygen* could be detected in the escaping gas, we must conclude that dissociation of NO_2 into NO and O_2 had not taken place, and, by implication, that nitrosyl chloride was not formed in these experiments.

Vapour-density determinations were performed exactly as before, except that the distillation of the vapour through the bulbs was continued for a *very considerable time*, the object being to ascertain, by the action of the escaping vapour on glacial acetic acid, whether free chlorine were present.

I do not consider this series of determinations to be as accurate as

the next (C), as, owing to the purpose just alluded to, the distillation was pushed so far that a considerable quantity of liquid condensed in the first bulb, which was only removed with great difficulty.

The glacial acetic acid through which the issuing vapours were bubbled was contained in a small distilling flask. After the operation, the acid had a deep crimson colour, which, however, completely disappeared when dry air was led through the acid for a short time at a temperature of 100°. A portion of the acid was then diluted, and nitric acid and silver nitrate added, the precipitate (a very small one) being filtered off. The liquid was subsequently treated with excess of potash, and after boiling for some time the solution was acidified with nitric acid. A considerable quantity of silver chloride remained undissolved.

It is therefore certain that a notable amount of chloracetic acid had been formed, even in ordinary daylight and at ordinary temperatures, from which fact we must draw the inference that free chlorine was almost certainly present in the vapours.

The following are the numbers for this series:—

SERIES B.—*Bulbs sealed at 24° and 761·7 mm.*

	I.	II.	III.
V_b	117·8	155	175·0 (approx.)
V_a	0·0	0·0	0·0
V_v	117·8	155	175
B_v	73·7767	60·8276	79·6245
B_a	73·5345	60·5154	79·2724
W_{v-a}	0·2422	0·3122	0·3521
W_a	0·14043	0·184775	0·20845
W_v	0·38263	0·496975	0·56055
V.D.	39·33	38·82	38·80
Cl per cent.	5·66	5·5	—

During the manipulation of bulb III, it was broken, and consequently no chlorine determination could be made. Its volume was taken as being approximately 1 c.c. less than in series A, in order to obtain an approximate vapour-density, as it was thought that possibly this might be useful.

Calculations were made as in series A, the nitrosyl chloride hypothesis being now excluded.

SERIES B.

	I.		II.	
	Densities.	Diff.	Densities.	Diff.
Found	39·33	—	38·82	—
Calc. hyp. β	41·63	2·30	41·64	2·82
,, ,, γ	41·70	2·37	41·73	2·91

There is here a slight difference in favour of β, but considering how small it is and how widely both series of calculated numbers vary from the observed density, the figures cannot be taken as proving anything.

C. The liquid for use in this series was prepared in the same way as for the last, but the distillation was allowed to go on for a *short time* only, in order that the most volatile portions of the vapour should have influence. Hence the large amount of unexpelled air and high percentage of chlorine.

SERIES C.—*Bulbs sealed at* 20·1° *and* 748·3 *mm.*

	I.	II.	III.
V_b	117·9	154·7	144
V_a	0·55	4·5	18·85
V_v	117·35	150·2	125·15
B_v	74·5864	60·4787	65·5103
B_a	74·3507	60·1814	65·2689
W_{v-a}	0·2357	0·2973	0·2414
W_a	0·13926	0·17824	0·14852
W_v	0·37496	0·47554	0·38992
$\frac{2}{5}$AgCl	0·1527	0·2206	0·2219
V.D.	38·87	38·51	37·9
Cl per cent.	25·12	28·68	35·11

The numbers in this series are, I think, fairly trustworthy, as everything worked very smoothly throughout.

The following are the calculated results:—

SERIES C.

	I.		II.		III.	
	Densities.	Diff.	Densities.	Diff.	Densities.	Diff.
Found.........	38·87	—	38·51	—	37·90	—
Calc. β	40·40	1·53	40·10	1·59	39·54	1·64
„ γ	40·88	2·01	40·70	2·19	40·50	2·60

Here there is a decided difference in favour of hypothesis β. The extreme variation in the differences is only 0·11, though it must be admitted that the differences themselves are rather large.

Now in the calculated values on hypothesis γ, the variation in the differences amounts to 0·59, and the whole series is from 0·48 to 0·96 farther from the truth than the other. These discrepancies are considerable, occurring as they do in a total difference never exceeding 2·6.

With regard to the uniform difference of 1·5 between the observed densities and the numbers obtained on hypothesis β, I think it is easily understood when we remember that Gibbs' formula is only approximate, and that a like variation, the same in direction and nearly the same in amount, was observed by Ramsay and Cundall in calculating the density of a similar mixture with the help of this formula.

From these experiments, I think we may reasonably conclude that direct combination of nitric peroxide and chlorine, like all the other methods, fails to yield nitryl chloride; the product hitherto regarded as such being merely a *solution* of chlorine in nitric peroxide, together with nitrosyl chloride, when the experiment is performed at a red heat.

In two samples of this product, prepared at 150° on different occasions, the chlorine was determined, and was found to be 8·6 and 9·2 per cent. respectively.

Now if a compound were formed, we should expect the amount of chlorine to vary in products formed at different rates and during different times. We must, therefore, I think, regard these numbers as expressing the *solubility* of chlorine in the peroxide at the temperature of the condenser, which varied probably from − 20° to − 15°.

Indeed, a solution containing 4·75 per cent. of chlorine was readily prepared by cooling the test-tube containing the peroxide during the passage of the chlorine, and though the solution was probably not saturated, nor was it so cold as in the spiral condenser, still the

liquid after this treatment strongly resembled that which dripped from the delivery tube of the condenser.

I must mention, however, that when endeavouring to prepare a specimen of this solution a few days ago for exhibition to the Society, the peroxide, though it absorbed the chlorine with great vigour, underwent no appreciable change of colour, nor was any such change induced when a portion of the liquid was warmed slightly. The temperature of the experiment was $-15°$, and the peroxide was quite free from water, as was shown by its solidifying during the passage of the chlorine.

I am inclined to think that a trace of moisture is necessary for the development of the red colour, which is probably due to a small quantity of nitrosyl chloride:—

$$Cl_2 + H_2O = 2HCl + O;\ HCl + (NO)NO_3 = NOCl + HNO_3.$$

In conclusion, I must render my hearty thanks to Dr. Tilden especially, and also to Dr. Nicol, for their ready and kindly help.

XXVI.—*On Sulphine Salts containing the Ethylene Radical.* Part I. *Diethylenesulphide-methyl-sulphine Salts.*

By Orme Masson, M.A., D.Sc., University of Edinburgh.

The discovery made by von Oefele in 1863 (this Journ., **17**, 106), that ethyl iodide and ethyl sulphide combine directly to form the iodide of a sulphine base, led to the investigation of the products of several similar reactions and to the establishment of many points of analogy between the sulphine salts and the salts of organic ammonium and phosphonium bases. Still, the chemistry of sulphines is as yet very incomplete. Nothing, for instance, is known of di- and tri-sulphines comparable to the di- and tri-ammoniums; and very little of monosulphines containing other than monad radicles. Attempts were, indeed, made by Dehn and by Cahours to prepare sulphines containing the ethylene radical very soon after the publication of von Oefele's research; but these attempts were not successful, though they led to other interesting results. Their work will be more specially dealt with in Part II of this paper; here it may suffice to state that the method which they both employed — the heating of ethylene bromide with an alkyl sulphide—was proved by Dehn to result in

double decomposition between the reagents, followed by combination of the alkyl sulphide with the alkyl bromide so formed :—

$$2C_2H_4Br_2 + 2(CH_3)_2S = (C_2H_4)_2S_2 + 4CH_3Br.$$
$$CH_3Br + (CH_3)_2S = (CH_3)_3SBr.$$

It occurred to me that ethylene sulphine salts might be obtained by acting on ethylene sulphide with the haloïd compound of methyl or ethyl, as in that case probably there would be no such tendency to double decomposition.

Constitution of Diethylene Disulphide.

There are in reality two distinct substances which have the empirical formula C_2H_4S. One of them, discovered by Löwig and Weidmann in 1840, and afterwards investigated by Crafts (*Annalen*, **128**, 220), is a white amorphous powder produced by the action of potassium sulphide on ethylene bromide. It is insoluble in all ordinary solvents, and cannot be volatilised without undergoing chemical change. Nothing is known of its true constitution. Very different from this is the diethylene disulphide discovered in 1863 quite independently by Crafts (*Annalen*, **124**, 120; **125**, 123) and Husemann (*Annalen*, **126**, 269). This is a white crystalline substance, soluble in alcohol, ether, benzene, and carbon disulphide, volatile even at ordinary temperatures, melting at 111°, and boiling at 200°. It is prepared from the amorphous sulphide by heating it at 160°, either alone or with carbon disulphide in sealed tubes; and I have found that it is also directly formed in considerable quantity, together with the amorphous sulphide, when strong alcoholic solutions of ethylene bromide and potassium sulphide are mixed. The following is a summary of what is known regarding its constitution.

Crafts, who regarded it as C_2H_4S, showed that it is a true sulphide, analogous to those of the alcohol radicals, by preparing its halogen and oxygen addition products. Thus he obtained the bromide $C_2H_4SBr_2$ by direct addition of bromine, the sulphoxide C_2H_4SO by decomposing the bromide with water and by the action of nitric acid on the sulphide itself, and the sulphone $C_2H_4SO_2$ by the further action of nitric acid. Husemann, however, ascertained that the vapour-density of the sulphide requires its formula to be doubled; and hence he represented it and its derivatives as $(C_2H_4)_2S_2$, $(C_2H_4)_2S_2Br_4$, $(C_2H_4)_2S_2O_2$, $(C_2H_4)_2S_2O_4$. If these formulæ are correct, it is evident that the molecule of the sulphide must be symmetrical, and must contain two dyad sulphur-atoms, conditions that are well fulfilled by the formula given in some of the text-books,

$$S{<}^{C_2H_4}_{C_2H_4}{>}S.$$

Dehn's theory (*Annalen*, Suppl. **4**, 83) that it is the sulphide of a sulphinic base, $(C_2H_4)_2S^{vi} : S''$, must be at once rejected; and the formula $C_2H_4 : S : S : C_2H_4$, suggested in *Watts' Dictionary* (**6**, p. 607), is equally incorrect, as it does not allow of the formation of a disulphone. Moreover, the constitution given above agrees well with two reactions which yield the sulphide, discovered by Husemann, viz., that between ethylene bromide and the mercury salt of ethylene mercaptan, and that between ethylene bromide and ethylene thiocarbonate :—

$$C_2H_4{<}^{S}_{S}{>}Hg + Br_2C_2H_4 = C_2H_4{<}^{S}_{S}{>}C_2H_4 + HgBr_2, \text{ and}$$

$$C_2H_4{<}^{S}_{S}{>}CS + Br_2C_2H_4 = C_2H_4{<}^{S}_{S}{>}C_2H_4 + CSBr_2,$$

(the thiocarbonyl bromide being represented by the products of its decomposition).

It is evident, however, that these reactions are quite compatible with the view that the sulphide is, as Crafts represented it, C_2H_4S; and that, since none of its derivatives *require* the double formula, the proof that it is $(C_2H_4)_2S_2$, and not C_2H_4S, has hitherto rested solely on the physical evidence of its vapour-density. Though this is generally accepted as sufficiently convincing, it is satisfactory to obtain corroborative chemical evidence such as is given in the following pages, where derivatives are described which do not admit of the halving of the formula $(C_2H_4)_2S_2$.

Preparation of Diethylene Disulphide.

The following method has been found to work easily for the preparation of this substance in quantity. Ethylene bromide, dissolved in about its own volume of alcohol, is mixed in a large flask with a concentrated solution of potassium sulphide, more than an equivalent quantity of the latter being employed. The flask is connected with a long upright condenser, and should be placed in a draught cupboard, as the odour evolved (due to the formation of the mercaptan and other bye-products) is extremely unpleasant. The action begins at once, the amorphous ethylene sulphide and potassium bromide being precipitated; and so much heat is developed that ebullition occurs in a very few minutes. When the reaction is over and the flask has become quite cold, enough water is added to give fluidity to its almost solid contents, the condenser is placed in the normal position, and a current of steam is led in by a tube dipping nearly to the bottom of the flask, which is at the same time heated on a sand-bath. The distillate which is collected consists at first of dilute alcohol con-

taining diethylene disulphide in solution. As the alcohol becomes weaker, the disulphide is seen to solidify in the condenser in the form of crystals, which are washed down into the receiver. The distillation is continued till no more of the disulphide passes over; the alcoholic distillate is then largely diluted with water; and the precipitated disulphide is collected and dried by pressing between folds of blotting-paper, and, finally, over sulphuric acid. The contents of the flask, which still contains the amorphous sulphide, are poured on to a filter; this is well washed with hot water, and dried at 100°.

The fact that the crystalline disulphide is produced by the reaction between ethylene bromide and potassium sulphide seems to have been overlooked by previous observers, who also appear to have been unaware of its convenient property of volatilising in the vapour of water or alcohol at a temperature much below its own boiling point (200°). That it is really produced simultaneously with the amorphous sulphide, and not from it by the action of the steam, is proved by the limited amount obtained, and by the fact that this change from the amorphous to the crystalline state does not occur below about 160°, either in a sealed tube containing water, or under any other known conditions.

The next step in the preparation is to induce this change in the amorphous product. Husemann recommended heating it in sealed tubes at 160° with carbon disulphide; but this is a troublesome operation, and altogether unnecessary. A fairly good yield is obtained by simply heating the amorphous powder in a large retort, the lower part of which dips into an oil-bath, provided that the temperature is raised very gradually and is then kept several hours at 160°, but not allowed to rise much above that temperature. The product sublimes into the upper part and neck of the retort, where it slowly forms a hard yellow glassy cake. A certain amount of charred matter remains at the bottom of the retort when the operation is over. The cake of crude disulphide is then shaken out, broken up, washed sparingly with alcohol, which frees it from most of its objectionable odour (due to an oily bye-product), and is distilled in a current of steam. After pressing and drying, it is quite white and pure, but the water remaining in the distilling flask contains much oily and disagreeably smelling impurity.

In one preparation, I used 650 grams of potash (converted into potassium sulphide) and 1000 grams of ethylene bromide; and obtained, in the first stage, 45 grams of the crystalline disulphide and 126 grams of the amorphous sulphide. This is 54 per cent. of the theoretical yield of C_2H_4S from $C_2H_4Br_2$ (319 from 1000); but better results were got on a smaller scale by the use of a larger excess of potassium sulphide. In the second stage, the 126 grams of

the amorphous compound gave 75 grams of pure diethylene disulphide; so that, in all, 120 grams of this substance were prepared from 1000 of ethylene bromide, that is, 37 per cent. of the theoretical yield.

Action of Methyl Iodide on Diethylene Disulphide.

It was not unnaturally expected that, if any combination of these two substances occurred, 1 mol. of the disulphide would combine with 2 mols. of methyl iodide, and that a sulphine salt would be formed of the constitution—

$$\begin{matrix}H_3C\\I\end{matrix}\!>\!S\!<\!\begin{matrix}C_2H_4\\C_2H_4\end{matrix}\!>\!S\!<\!\begin{matrix}CH_3\\I\end{matrix}.$$

This, however, does not take place; for only 1 mol. is taken up, even when a large excess of the iodide is employed. The salt produced is the iodide of a base which may be viewed as trimethylsulphine in which two of the methyl-groups are displaced by the dyad radical, $S(C_2H_4)''_2$,—a view that is best expressed by the name *diethylene-sulphide-methyl-sulphine*:—

$$\begin{matrix}H_3C\\H_3C\end{matrix}\!>\!S\!<\!\begin{matrix}CH_3\\I\end{matrix} \qquad\qquad S\!<\!\begin{matrix}C_2H_4\\C_2H_4\end{matrix}\!>\!S\!<\!\begin{matrix}CH_3\\I\end{matrix}$$

Trimethylsulphine iodide. Diethylenesulphide-methyl-sulphine iodide.

Such a base should resemble trimethylsulphine in its general characters, but should differ from it in certain respects on account of the comparatively negative character of the $S(C_2H_4)_2$ group; which ought to impress itself (so to speak) on the whole molecule. This, as will be shown, is actually the case.

The reaction occurs slowly at the ordinary temperature. When ethereal solutions of the two substances are mixed in a flask and set aside for some weeks, minute crystals of the sulphine iodide gradually separate and form a crust on the sides of the flask. At a temperature of about 70°, however, the reaction is completed more rapidly. The mixture of diethylene disulphide and methyl iodide (the latter in slight excess of the theoretical quantity) is heated for about 12 hours at that temperature in sealed tubes placed in a water-bath. Some pressure is developed, and a combustible gas escapes when the tubes are opened, after cooling. The crude product of the reaction is a solid reddish-coloured mass, and consists of a mixture of two substances,—the iodide and the tri-iodide of diethylenesulphide-methyl-sulphine. After the excess of methyl iodide has been got rid of by powdering in a mortar and exposure to the air, these two salts may be separated by washing with boiling alcohol, which dissolves out the dark-red triiodide and leaves the white iodide unaffected; or

the whole mass may be treated with a somewhat large volume of boiling water, which dissolves the iodide and throws down the triiode as a black tarry precipitate. The solution is filtered, and is then boiled in a beaker till it has lost its yellow colour and been reduced to a comparatively small bulk; but the evaporation must not be carried so far as to cause decomposition. On cooling, it deposits a plentiful crop of opaque white apparently cubical crystals; and successive crops of these may be obtained by alternate evaporation and cooling of the mother-liquor. The total yield of iodide obtained in this way is nearly equal to double the weight of the diethylene disulphide employed.

Diethylenesulphide-methyl-sulphine Salts.

The *iodide*, $C_5H_{11}S_2I$. After being purified by recrystallisation from hot water, the salt was analysed with the following results:—

I. 0·2087 gram gave 0·1745 gram of CO_2 and 0·0818 gram of H_2O.
II. 0·1981 " 0·1662 " 0·0775 "
III. 0·1793 gram gave 0·3142 gram of $BaSO_4$, after ignition with a mixture of sodium carbonate and potassium chlorate.
IV. 0·1993 gram gave 0·1783 gram of AgI.

	Calculated for $C_5H_{11}S_2I$.	Found. I.	II.	III.	IV.
C	22·90	22·80	22·88	—	—
H	4·20	4·30	4·35	—	—
S	24·42	—	—	24·07	—
I	48·48	—	—	—	48·35
	100·00				

The salt is readily soluble in hot water, much less so in cold water, very sparingly in alcohol, and insoluble in ether. From hot water, it crystallises in opaque white apparently cubical crystals; but the cold aqueous solution evaporated in a vacuum deposits it in the form of transparent needles. The aqueous solution undergoes some decomtion when evaporated to dryness at 100°. The dry salt sublimes without melting when heated somewhat above 100°; and is at the same time completely decomposed, partly, at any rate, into its original constituents, for crystals of diethylene disulphide are formed in the upper part of the vessel in which the operation is conducted. In this decomposition, the behaviour of the salt is analogous to that of trimethylsulphine iodide. Towards silver salts, it also conducts itself in a similar manner, giving silver iodide and a new salt of the sulphine base. In order, however, to obtain the hydroxide by the

action of moist silver oxide, it is necessary to operate on a very dilute cold solution of the iodide; for the reaction will not take place in a strong cold solution, and any application of heat at once decomposes the base with the formation of silver sulphide and a disagreeably smelling volatile liquid. It is therefore more convenient to prepare the other salts by acting on the iodide with the corresponding salt of silver or on the sulphate (so obtained) with the corresponding barium salt.

The *triiodide*, $C_5H_{11}S_2I_3$, which, as already stated, occurs as a bye-product in the formation of the iodide, is easily obtained by the direct combination of the latter salt with iodine. For this purpose, the calculated quantities are weighed out, the iodide is dissolved in sufficient hot water, and the iodine in sufficient hot alcohol, and the two are mixed. When the solution cools, it deposits the triiodide in the form of very thin plates of a lustrous garnet-red colour. They may be purified by washing with ether and recrystallising from hot alcohol. The following are the results of analysis:—

I. 0·4255 gram gave 0·1821 gram of CO_2 and 0·0835 gram H_2O.
II. 0·4364 gram, after treatment with sulphurous acid solution, gave 0·5958 gram of AgI.

	Calculated for $C_5H_{11}S_2I_3$.	Found. I.	Found. II.
C	11·63	11·65	—
H	2·13	2·18	—
S	12·40	—	—
I	73·84	—	73·79
	100·00		

The salt is insoluble in ether, only slightly soluble in cold alcohol, freely in hot alcohol. When warmed with water, it melts and aggregates into heavy black oily drops; these gradually decompose, on boiling, into the original iodide and iodine. Sulphurous acid solution acts on it as on a mixture of these substances. When heated by itself it melts at about 89°; and at about 145° it begins to evolve a brown oily distillate, whilst at a still higher temperature a white crystalline sublimate and iodine vapour are formed. Ammonia solution at once converts it into a black amorphous substance which explodes when heated, but not so violently as does iodide of nitrogen, to which it bears a close resemblance.

The formation of this triiodide in the preparation of the iodide is partly, no doubt, accounted for by the presence of free iodine in the methyl iodide employed; but to a larger extent it must be due to a

secondary action, which gives rise also to the combustible gas whose presence is always noticed on opening the tubes.

Two distinct views are possible as to the constitution of this substance. The first would represent it as formed by the union of iodine with the dyad sulphur-atom; in which case it would be analogous to the tetrahaloïd derivatives of diethylene disulphide, thus:—

$$I_2S{<}{}^{C_2H_4}_{C_2H_4}{>}SI_2 \qquad\qquad I_2S{<}{}^{C_2H_4}_{C_2H_4}{>}S{<}{}^{CH_3}_{I}$$

Diethylene-disulphide tetr-iodide. Diethylene-disulphide-methyl-sulphine tri-iodide.

As is well known, however, various organic bases in whose molecules there are no atoms comparable to this second sulphur-atom, form polyiodides; and it was shown by Dr. Dobbin and myself (Trans., 1885, 56) that trimethylsulphine iodide combines directly with iodine, bromine, and chlorine to form definite crystalline compounds of the general formula $(CH_3)_3SX_3$. Now the salt under consideration so exactly resembles these compounds in its properties (more particularly in its behaviour with water and with ammonia), that it seems right to conclude that its constitution is similar to theirs (as yet not determined with certainty), and that it should be represented in the mean time as $S(C_2H_4)_2S(CH_3)I,I_2$, not as $I_2S(C_2H_4)_2SCH_3I$.

In this connection, it appeared to be a matter of some interest to ascertain whether the iodide would combine in a similar manner with bromine and chlorine. According to the view of its constitution taken in this paper, viz., that it is trimethylsulphine iodide in which two methyl-groups are displaced by the comparatively negative group $S(C_2H_4)''_2$ one would expect it to show less tendency than trimethylsulphine iodide itself to combine with strongly negative radicals such as the halogens. This is confirmed by experiment. Dry bromine vapour passed over the salt is absorbed, the white iodide assuming a scarlet colour, but without melting (in the case of trimethylsulphine iodide much heat is developed and the salt melts); but this scarlet product is not very stable, for it decomposes in the air, and rapidly when heated with alcohol or water, in which last case a solution of the sulphine bromide is obtained. Chlorine, on the other hand, has absolutely no action on the iodide if both are dry; whilst it combines very energetically with dry trimethylsulphine iodide.

The *nitrate*, $C_5H_{11}S_2NO_3$, is obtained by mixing a solution of silver nitrate with that of the iodide. The point of exact equivalency can be very nearly hit by observing the colour of the silver precipitate, which changes from a yellowish-white to a distinct yellow as soon as sufficient silver nitrate has been added. The aqueous solution under-

goes some decomposition when evaporated to dryness; but the product is easily purified by crystallisation from hot alcohol.

0·2924 gram gave on combustion 0·3232 gram CO_2 and 0·1561 gram H_2O.

	Calculated for $C_5H_{11}S_2NO_3$.	Found.
C................	30·46	30·15
H................	5·58	5·93

The nitrate is very soluble in water, but is not deliquescent. It is much less soluble in cold alcohol than in hot, and is insoluble in ether. It separates in the form of thin pearly plates when the hot alcoholic solution is cooled or when ether is added to the cold alcoholic solution; whilst by slow evaporation it is obtained in large apparently rhombic crystals. It melts at 172°, and at once begins to decompose, a crystalline sublimate being formed.

The *silver salt*, $C_5H_{11}S_2NO_3,AgNO_3$, is obtained by mixing a strong solution of the nitrate with an excess of silver nitrate and then precipitating with alcohol. It forms small colourless barb-like crystals. It blackens on exposure to sunlight, and detonates slightly when heated. It is extremely soluble in water, less so in alcohol, and insoluble in ether.

0·1517 gram on ignition left a residue of 0·0449 gram of Ag.

	Calculated for $C_5H_{11}S_2NO_3,AgNO_3$.	Found.
Ag................	29·43	29·60

The *sulphate*, $2(C_5H_{11}S_2)_2SO_4,7H_2O$. The salt is obtained by treating the iodide with silver sulphate solution, evaporating the filtered liquid to a syrup, dissolving this in strong alcohol, and either precipitating with ether or crystallising out in a vacuum. It is a remarkable fact that throughout this treatment the salt retains its water of crystallisation; indeed it does not appear capable of parting with it in any circumstance without undergoing further change. The decomposition produced by evaporation of the aqueous solution at 100° is greater in the case of the sulphate than in those of the other salts; it results in the formation of a flocculent white insoluble substance, free sulphuric acid, and a volatile sulphur compound having a very nauseous odour. There will be occasion again to mention this odour and the substance which gives rise to it. The sulphate crystallises in large deliquescent prisms when the aqueous solution is slowly evaporated over sulphuric acid in a vacuum, in small needles when the alcoholic solution is similarly treated, and in large feathery groups when ether is allowed to diffuse down into the cold alcoholic solution. When heated, it melts with decomposition at

127°, water being given off together with diethylene disulphide and other volatile matters; and at a higher temperature charring occurs.

I. 0·2470 gram gave 0·2512 gram CO_2 and 0·1471 gram H_2O.
II. 0·2457 „ 0·2476 „ 0·1451 „
III. 0·3644 „ 0·3693 „ 0·2149 „
IV. 0·2508 gram gave 0·1381 gram $BaSO_4$ by precipitation with barium chloride.
V. 0·2425 gram, treated in the same manner, gave 0·1324 gram $BaSO_4$.

	Calculated for $2(C_5H_{11}S_2)_2SO_4,7H_2O$.	Found.				
		I.	II.	III.	IV.	V.
C......	27·97	27·73	27·48	27·64	—	—
H.....	6·76	6·62	6·56	6·55	—	—
S......	29·84	—	—	—	—	—
SO_4....	22·38	—	—	—	22·68	22·55
O......	13·05	—	—	—	—	—
	100·00					

Different preparations were used in this analysis, but both were from alcoholic solution. III and V were with one preparation; I, II, and IV with another. The hydrogen is obviously too low; but the formula given agrees much better than any other with the figures obtained.

The *chloride*, $C_5H_{11}S_2Cl$, may be prepared from the sulphate by exact precipitation with barium chloride and evaporation of the filtered solution. It is readily soluble in water, but slightly so in alcohol, and insoluble in ether. The hot saturated aqueous solution deposits a magma of needles on cooling; whilst the salt is obtained in the form of large transparent tables by the slow evaporation of the cold aqueous solution. It is not deliquescent.

0·2393 gram gave 0·2011 gram AgCl.

	Calculated for $C_5H_{11}S_2Cl$.	Found.
Cl	20·82	20·86 per cent.

Further analysis was not considered necessary, more especially as the platinichloride* has been fully analysed.

The chloride forms several characteristic compounds with metallic salts. Of these the platinum, gold, and mercury compounds have been examined.

Platinum salts.—Diethylenesulphide-methyl-sulphine chloride reacts

* The term "platinichloride," as being more systematic, is here applied to the compounds containing *platinic* chloride, $PtCl_4$.

with platinic chloride in a peculiar and interesting manner. As many as four distinct salts have been prepared and analysed. Of these four, three are direct compounds of $C_5H_{11}S_2Cl$ with $PtCl_4$ in different proportions, whilst the fourth is a similar compound *minus* the elements of hydrochloric acid. The salts are—

	Salt.	Chlorine ratio.
I	$2C_5H_{11}S_2Cl,PtCl_4$	1 : 2
II	$4C_5H_{11}S_2Cl,3PtCl_4$	1 : 3
III	$C_5H_{11}S_2Cl,PtCl_4$	1 : 4
IV	$C_{10}H_{21}S_4Pt_2Cl_9$	—

It is obvious that the first three, as judged by the ratio of the chlorine in the one half of the molecule to that in the other, form a definite series, whilst the fourth is quite distinct in character. If judged by their properties, however, the salts must be differently grouped; for the second, third, and fourth are insoluble amorphous yellow powders, whilst the first is orange-coloured, crystalline, and soluble.

The *platinichloride*, $2C_5H_{11}S_2Cl,PtCl_4$, is obtained as a heavy orange crystalline powder when a cold strong solution of the sulphine chloride is precipitated with platinic chloride. The salt is insoluble in alcohol and ether; sparingly soluble in cold water. It cannot be dissolved in hot water, as this converts it into the insoluble salt $C_{10}H_{21}S_4Pt_2Cl_9$; but it may be dissolved unchanged, in part at any rate, in a hot aqueous solution of the sulphine chloride; and from such a solution it separates on cooling in the form of groups of interlacing golden-yellow needles. The cold aqueous solution deposits, on standing, an insoluble amorphous yellow powder, which was found to contain, in one instance, 36·35 per cent. of platinum, and is most probably a mixture of the salts $C_5H_{11}S_2Cl,PtCl_4$ (which requires 38·42 per cent.) and $4C_5H_{11}S_2Cl,3PtCl_4$ (which requires 34·55 per cent.). Analysis of the platinochloride gave the following results:—

I. 0·4264 gram gave on combustion 0·2714 gram CO_2 and 0·1277 gram H_2O, and left a residue of 0·1232 gram Pt.

II. 0·2512 gram gave 0·0720 gram Pt.

III. 0·4537 „ 0·1303 „

IV. 0·2535 gram, ignited with sodium carbonate, gave 0·3188 gram AgCl.

V. 0·2991 gram, ignited with sodium carbonate and potassium chlorate, gave 0·4076 gram $BaSO_4$.

	Calculated for $2C_5H_{11}S_2Cl,PtCl_4$.	Found. I.	II.	III.	IV.	V.
C	17·70	17·36	—	—	—	—
H	3·24	3·33	—	—	—	—
S	18·88	—	—	—	—	19·06
Pt*	28·76	28·89	28·67	28·72	—	—
Cl	31·42	—	—	—	31·11	—
	100·00					

Before being analysed, the crystalline precipitate was washed on a filter with cold water, alcohol, and ether, and dried at the ordinary temperature in a vacuum. When it has been freed from moisture in this way, it may safely be heated at 100°; above 130°, it turns black and decomposes without melting.

The salt $C_{10}H_{21}S_4,Pt_2Cl_9$ is produced, as stated above, when the platinichloride is digested with boiling water. The orange salt at once loses its crystalline character and assumes the appearance of a yellow amorphous insoluble powder. The aqueous filtrate from this has a distinctly acid reaction, due to free hydrochloric acid. Evaporated to dryness on the water-bath, it yields a crystalline residue of diethylenesulphide-methyl-sulphine chloride, which is readily identified by its reactions with the chlorides of gold, platinum, and mercury, by boiling it with soda solution (see later). The reaction which occurs may, therefore, be expressed by the equation—

$$2(2C_5H_{11}S_2Cl,PtCl_4) = C_{10}H_{21}S_4Pt_2Cl_9 + HCl + 2C_5H_{11}S_2Cl.$$

The analysis of the insoluble salt gave the following results:—

I. 0·2874 gram gave 0·1287 gram CO_2 and 0·0611 gram H_2O.
II. 0·2656 „ 0·1050 „ Pt.
III. 0·2271 „ 0·0898 „ „
IV. 0·2510 gram, ignited with lime, gave 0·3294 gram AgCl.

	Calculated for $C_{10}H_{21}S_4Pt_2Cl_9$.	Found. I.	II.	III.	IV.
C	12·26	12·21	—	—	—
H	2·15	2·36	—	—	—
S	13·09	—	—	—	—
Pt	39·85	—	39·53	39·54	—
Cl	32·65	—	—	—	32·47
	100·00				

The two salts, $4C_5H_{11}S_2Cl,3PtCl_4$ and $C_5H_{11}S_2Cl,PtCl_4$, both of

* The atomic weight of platinum is taken as 195.

which are insoluble amorphous yellow powders, closely resembling the salt $C_{10}H_{21}S_4Pt_2Cl_9$ in appearance and properties, are thrown down as a mixed precipitate when platinic chloride is added to a hot solution of the sulphine chloride. Such a precipitate was found to contain 37·61 and 37·70 per cent. of platinum. Digesting it with boiling water and with alcohol did not affect its composition. As the formula $C_5H_{11}S_2Cl,PtCl_4$ requires 38·42 per cent. of platinum, this precipitate was suspected of containing it together with some impurity; an attempt was therefore made to obtain it in a pure condition by fractional precipitation. Accordingly, a weighed quantity of the pure sulphine chloride was dissolved in boiling water, and hot platinic chloride solution—an amount very nearly equal to that calculated for the formation of the salt $C_5H_{11}S_2Cl,PtCl_4$—was added in four successive equal portions. The first two fractions, taken together, gave 34·14 per cent. of platinum; the third gave 34·06; and the fourth, 34·26. The orange-coloured filtrate from this last fraction was again boiled, when it almost at once threw down a fifth precipitate, larger than all the rest put together, and of a slightly different shade of yellow. This, on analysis, proved to be the salt $C_5H_{11}S_2Cl,PtCl_4$, in a fairly pure state.

I. 0·2976 gram gave 0·1242 gram CO_2, 0·0632 gram H_2O, and 0·1141 gram Pt.
II. 0·1957 gram gave 0·0751 gram Pt.
III. 0·2151 gram, ignited with lime, gave 0·2966 gram AgCl.

	Calculated for $C_5H_{11}S_2Cl,PtCl_4$.	Found. I.	II.	III.
C........	11·82	11·38	—	—
H........	2·17	2·36	—	—
S........	12·61	—	—	—
Pt........	38·42	38·34	38·37	—
Cl........	34·98	—	—	34·11
	100·00			

The smaller fractions, after the separate platinum determinations had shown them to have practically the same composition, were mixed for further analysis.

I. 0·2558 gram gave 0·1364 gram CO_2 and 0·0638 gram H_2O (the platinum was lost).
II. 0·1946 gram, ignited with lime, gave 0·2620 gram AgCl.
III, IV, and V (separate fractions), 0·1245, 0·1324, and 0·1608 gram respectively gave 0·0425, 0·0451, and 0·0551 gram Pt.

	Calculated for $4C_5H_{11}S_2Cl_4,3PtCl_4$.	Found. I.	II.	III.	IV.	V.
C	14·18	14·54	—	—	—	—
H	2·60	2·77	—	—	—	—
S......	15·12	—	—	—	—	—
Pt.....	34·55	—	—	34·14	34·06	34·26
Cl	33·55	—	33·30	—	—	—
	100·00					

The substance was thus proved to be the salt $4C_5H_{11}S_2Cl,3PtCl_4$ in a nearly pure condition.

These amorphous salts are practically insoluble in alcohol, ether, water (hot or cold), and dilute acids. They are slightly soluble in hot strong hydrochloric acid, and in strong aqueous ammonia, and still more so in hot strong nitric acid; but they cannot be obtained from these solutions in the crystalline state. Cold solution of hydric sulphide does not affect them; but if they are suspended in water at 100° and submitted to the action of a current of the gas, they are completely decomposed, platinic sulphide being formed. Ammonium sulphide causes a similar decomposition at the ordinary temperature. They behave like the orange salt when heated, turning black, and quietly evolving volatile matter without melting.

The *aurichloride*, $C_5H_{11}S_2Cl,AuCl_3$, is a light yellow amorphous powder, thrown down when gold chloride is added to a cold solution of diethylenesulphide-methyl-sulphine chloride. When heated with water, it dissolves, but is at once decomposed; and there gradually separate, not crystals of the salt, but minute yellow spangles of metallic gold. These impart to the liquid a greenish tinge, when looked at by transmitted light. This forms a very characteristic test for the chloride.

0·1808 gram gave on ignition 0·0761 gram Au.

	Calculated for $C_5H_{11}S_2Cl,AuCl_3$.	Found.
Au	41·50	42·09

The *mercury salt*, $C_5H_{11}S_2Cl,HgCl_2$, is produced as a crystalline white precipitate, when strong aqueous solutions of the two constituents are mixed. It may be recrystallised from hot water, when it separates in the form of needles mixed with thin plates.

0·6191 gram gave 0·3318 gram of HgS.

	Calculated for $C_5H_{11}S_2Cl,HgCl_2$.	Found.
Hg	45·30	46·20

The *hydroxide*, $C_5H_{11}S_2 \cdot OH$, has not been isolated; but a solution of it is formed when a cold and very dilute solution of the iodide is shaken with recently precipitated silver oxide. It has an alkaline reaction, and acts like an alkali on the salts of the heavy metals. It cannot be boiled without undergoing decomposition; the products are an insoluble white flocculent matter and a volatile sulphur compound with a peculiarly disagreeable odour, the same that has already been mentioned as characterising the decomposition of the sulphate and occurring when a solution of the iodide is warmed with silver oxide.

In order to investigate these decomposition products of the hydroxide, a solution of a weighed quantity of the sulphate was mixed with a slight excess of barium hydroxide, and filtered, without the application of heat. The filtrate quickly developed the peculiar odour, which gradually increased in intensity; and after it had stood for some hours drops of an oily liquid began to separate out, thus showing that the hydroxide decomposes slowly, even at the ordinary temperature. The liquid was then distilled. The decomposition became complete just before the boiling point was reached, and it was marked by the appearance of a sudden white turbidity in the liquid. The oil all came over with the distillate; and the residual liquid in the flask contained a small quantity of a bulky white flocculent substance.

For analysis, the oil was simply dried with calcium chloride and filtered, as it was found that it could not be distilled alone at the atmospheric pressure without decomposition. The results obtained point to the formula $C_{12}H_{24}S_5$.

I. 0·2664 gram gave 0·4257 gram CO_2 and 0·1806 gram H_2O.
II. 0·2460 „ 0·3927 „ 0·1638 „
III. 0·2620 gram, after ignition with sodium carbonate and mercuric oxide, gave 0·9352 gram $BaSO_4$.

	Calculated for $C_{12}H_{24}S_5$.	Found. I.	II.	III.
C	43·90	43·58	43·54	—
H	7·32	7·53	7·40	—
S	48·78	—	—	48·81
	100·00			

It is a mobile, highly refractive, colourless, very disagreeably smelling liquid, not miscible with water, but soluble in alcohol and ether. Its sp. gr. is 1·044 at 16° (water at 15·5° = 1). Its reaction is neutral. When heated to 150°, it decomposes, becoming dark in colour, without ebullition. It may, however, be readily volatilised in a current of steam. It is violently attacked by nitric acid, which

oxidises it first to a substance of the nature of a sulphone, and then, by further action, to sulphuric and oxalic acids. It is readily acted on by chlorine-water and bromine-water, with the formation of yellow or red resinous substances. It also combines with methyl iodide, the product being a syrupy liquid, which cannot be induced to crystallise.

The white amorphous decomposition-product of the hydroxide, formed at the same time as the oil, was collected on a filter, washed with dilute hydrochloric acid and with water, and dried. The bulky appearance that it presented while suspended in water was most misleading, for its total quantity proved to be very small—too small to permit of an analysis being made. It melts when heated on platinum foil, evolves a sulphide odour, and then burns with a blue flame, leaving no residue. It is evidently, therefore, an organic sulphur compound; in appearance, it resembles the amorphous ethylene sulphide. Though it is produced in such small quantity, its formation is a constant and apparently necessary accompaniment to that of the oil, and a knowledge of its nature is required before an equation can be given for the decomposition of the hydroxide.

Action of Alkalis on the Salts of Diethylenesulphide-methyl-sulphine.—If a solution of the iodide, chloride, sulphate, or nitrate, be heated with potash, phenomena occur of a precisely similar nature to those just described as resulting from the action of heat on the hydroxide. The clear solution becomes suddenly turbid at a temperature near the boiling point; and the oil, $C_{12}H_{24}S_5$, distils over with the steam. The change also occurs slowly at the ordinary temperature. Baryta-water acts on the soluble salts in the same manner, but less readily. From this it must be inferred that alkalis are capable of turning out the sulphine base from its salts, or, to speak more accurately, of entering into double decomposition with those salts. This reaction not only affords a most convenient and delicate test for the sulphine radical (the smell of the oil being unmistakeable), but marks a distinction of some theoretical interest between it and the trimethylsulphine radical; for it is well known that the salts of the latter are not attacked by alkalis, in which respect, as in many others, they resemble the tetramethyl-ammonium and tetramethyl-phosphonium salts. But this difference between the two sulphines is just what might be expected if the view of the constitution of the diethylene-sulphide-methyl-sulphine salts that is expressed in the name given to them be correct; for it involves the assumption that their base is less positive than that of the trimethylsulphine salts, though in most respects strictly analogous to it.

It has already been mentioned that ethylene sulphide occurs in two

distinct forms, the crystalline disulphide, $(C_2H_4)_2S_2$, and the amorphous variety, whose constitution is unknown, and which may be therefore written $(C_2H_4)_nS_n$. The n may be 1, or may be more than 2; that is to say, the change which occurs when the disulphide is produced from it by the action of heat may be a polymerisation, or a breaking up of the molecule. It occurred to me that a test between these two possibilities might be afforded by the action of methyl iodide on the amorphous sulphide. If it be C_2H_4S, and if combination occurs at all, one would certainly expect a sulphine salt of the constitution $C_2H_4 = S <^{CH_3}_{I}$ to be formed. This salt and its derivatives would probably possess very similar properties to the trimethylsulphine salts, from which they would also differ very little in composition. If, on the other hand, the amorphous sulphide be more complex than the crystalline one, a totally different result might be expected. It has been shown that $(C_2H_4)_2S_2$ can combine readily with CH_3I, but not with $2CH_3I$; and it is but reasonable to conclude that $(C_2H_4)_nS_n$, where n is greater than 2, would behave in an analogous manner, and that some of the sulphur-atoms in the molecule would remain unaffected by the reaction. Of course the action must take place, to be of any value as a test, at a temperature below that at which the change from one form of sulphide to the other is known to occur, *i.e.*, below about 160°.

A preliminary experiment has shown that action occurs readily at 60—70° in a sealed tube. A combustible gas and tarry products are formed; but, in addition to these, a sulphine iodide is produced which may be extracted by warm water, and freed from impurities by filtration with animal charcoal. The salt obtained by evaporation of the solution does not at all resemble diethylenesulphide-methyl-sulphine iodide in solubility or crystalline form, but does bear a close resemblance to the iodide of trimethylsulphine. I hope to be able to investigate the reaction fully.

XXVII.—*On Sulphine Salts containing the Ethylene Radical. Part II. Dehn's Reaction between Ethylene Bromide and Ethyl Sulphide.*

By Orme Masson, M.A., D.Sc.

In 1865 Dehn published (*Annalen*, Suppl. 4, 83) an account of the action which occurs when ethylene bromide and ethyl sulphide are heated together with water in sealed tubes. In the same year,

Cahours (*Annalen*, **136**, 151; and *Compt. rend*, **60**, 1147) described the action of methyl sulphide on ethylene bromide. They arrived, however, at very different conclusions; for, whilst Cahours stated that a disulphine salt of the constitution $(CH_3)_4(C_2H_4)S_2Br_2$ is produced, Dehn observed no such product of direct union. According to him, the main reaction consists in double decomposition by which ethyl bromide and diethylene disulphide are formed—

$$\text{I. } 2C_2H_4Br_2 + 2(C_2H_5)_2S = (C_2H_4)_2S_2{}^* + 4C_2H_5Br,$$

and this is accompanied by the union of part of the ethyl bromide with ethyl sulphide to form triethylsulphine bromide—

$$\text{II. } C_2H_5Br + (C_2H_5)_2S = (C_2H_5)_3SBr.$$

Returning to the subject in 1869 (*Ber.*, **2**, 479), Dehn stated that he had repeated his experiments with similar results, using methyl sulphide in place of ethyl sulphide; and he accordingly asserted that Cahours' supposed disulphine salt was in reality only trimethylsulphine bromide. This was afterwards, in 1875, acknowledged by Cahours to be the case (*Compt. rend.*, **80**, 1317; also *Ann. Chim. Phys.* [5], **10**, 13), and he fully confirmed Dehn's statement as to the formation of diethylene disulphide and triethyl(or methyl)sulphine bromide as the main products of the reaction. It is necessary to mention these facts, as descriptions of the purely imaginary salt, $(CH_3)_4(C_2H_4)S_2Br_2$, occur in some of our dictionaries of chemistry.

According to Dehn, the two equations given above do not represent the whole reaction; for in addition to the triethylsulphine bromide there are formed the bromides of two other sulphine bases, but in much smaller quantity than the former. His complete scheme for the reaction includes the equations—

$$\text{III. } C_2H_4Br_2 + (C_2H_5)_2S = (C_2H_4)(C_2H_5)_2SBr_2,$$
$$\text{IV. } C_2H_4Br_2 + C_2H_4S = (C_2H_4)_2SBr_2.$$

That is to say, there are formed side by side three distinct sulphine salts, one of which is of the ordinary kind containing tetrad sulphur, whilst the others are of a different character and contain hexad sulphur. In his second paper (*Ber.*, **2**, 479), Dehn states that he regards the formation of the salt, $(C_2H_4)(C_2H_5)_2SBr_2$, as proved by his experiments, and that of $(C_2H_4)_2SBr_2$ as not absolutely proved, but shown to be very probable. Cahours, in his later papers, corroborated Dehn as to the formation in small quantity of at least one other sulphine compound besides triethylsulphine bromide. He did not himself investigate this product, but he expressed a doubt as to the

* Dehn wrote the formula C_2H_4S, but his description of the substance shows it to have been the disulphide.

accuracy of Dehn's view of its constitution, a view, however, which he most strangely misrepresented.

As regards equation IV, one thing is at once obvious, that it involves a neglect of the fact that it is diethylene disulphide, $(C_2H_4)_2S_2$, and not a substance of the formula C_2H_4S, that, according to Dehn's own showing, results from the primary reaction. Other considerations, however, combine to make it difficult to accept Dehn's theory concerning these secondary products. It is based upon the idea that a class of sulphin*ic* salts can exist, resembling the sulphin*ous* salts in their general characters, and standing to them in a relation similar to that of sulphuric anhydride to sulphurous anhydride. This view, though plausible enough in 1865, is considerably weakened by the fact that no additional evidence of its truth has been published since that date. Indeed, if his theory be really a correct one, Dehn's salts stand alone, and occupy a position of very considerable importance to the student of sulphur compounds. This was recognised by Divers, who, in a recent paper bearing on the atomicity of sulphur (Trans., 1885, 213), referred to Dehn's salts, and to the halogen addition products of trimethylsulphine (described by Dobbin and myself) as exceptions—and apparently the only ones—to his rule that sulphur is never more than tetrad. The latter exception is, as yet, at any rate, a somewhat doubtful one; and I believe that the sequel will show that Dehn's salts need form no exception at all.

Dehn was unable to isolate and examine the bromides themselves; and a perusal of his paper shows that his theory of their constitution rests entirely on the properties and partial analyses of their platinichlorides. The question to be answered therefore resolves itself into this:—Is there sufficient reason for believing that these salts were respectively $(C_2H_4)(C_2H_5)_2S^{vi}Cl_2,PtCl_4$ and $(C_2H_4)_2S^{vi}Cl_2,PtCl_4$, as he represented them, or is it possible to substitute for these formulæ others more in keeping with the experimental evidence and with general probability?

His method of procedure was as follows:—The cold dilute aqueous solution of the mixed sulphine bromides, freed from diethylene disulphide and ethyl bromide, was shaken with recently prepared silver oxide, and the resulting mixture of hydroxides was treated with excess of hydrochloric acid, warmed, and fractionally precipitated with solution of platinic chloride. The triethylsulphine salt, being soluble in hot water, was the last to form. The first salts precipitated were yellow powders, apparently crystalline, practically insoluble in cold or hot water and in dilute acids, but somewhat soluble in strong aqueous ammonia. They were not acted on by hydrogen sulphide in the cold, but were decomposed by a stream of the gas when suspended in hot water.

The first two fractions of this insoluble precipitate contained 39·13 and 38·39 per cent. of platinum. Dehn's formula, $(C_2H_4)_2SCl_2,PtCl_4$, requires 39·31 per cent. (taking Pt as 195). There was not sufficient material for further analysis. The subsequent fractions had a constant composition, which, as tested by determination of the carbon, hydrogen, and platinum, agreed fairly well with that calculated from the formula $(C_2H_4)(C_2H_5)_2SCl_2,PtCl_4$.

As this is all the actual evidence brought forward by Dehn in proof of his theory of the existence of the sulphinic salts, that theory must fall if it can be shown that there is *a priori* ground for believing that these platinum salts had altogether different formulæ, and also that Dehn's own analyses agree as well, or better, with these formulæ than they do with his own.

As regards the first point. The properties of Dehn's platinum salts are strikingly unlike those of most platinichlorides, but are identical with those of the salt $(C_2H_4)_2S_2(CH_3)Cl,PtCl_4$, described in the last paper (p. 245) except in so far as "apparently crystalline" differs from "amorphous." This salt, like Dehn's, is an insoluble yellow powder thrown down when a hot solution containing the parent sulphine chloride is precipitated with platinic chloride. The iodide corresponding to it is formed by the union of diethylene disulphide $(C_2H_4)_2S_2$ with methyl iodide. It is not unnatural to suppose that the same sulphide will unite, though less energetically and completely, with ethyl bromide and even with ethylene dibromide. If these analogous reactions can occur, they will give rise to sulphine salts of the formulæ—

$$S{<}^{C_2H_4}_{C_2H_4}{>}S{<}^{C_2H_5}_{Br} \quad \text{and} \quad S{<}^{C_2H_4}_{C_2H_4}{>}S{<}^{C_2H_4}_{Br\,Br}{>}S{<}^{C_2H_4}_{C_2H_4}{>}S.$$

Diethylenesulphide-ethylsulphine bromide. Diethylenesulphide-ethylene-disulphine bromide.

In Dehn's reaction, as we have seen, diethylene disulphide is formed as a product of the first change: it is formed together with ethyl bromide and in the presence of ethylene bromide, and amidst conditions of temperature, &c., specially devised to favour such combinations. If, therefore, the salts whose formulæ are given above are capable of being produced, they would certainly be formed in Dehn's experiment. The platinum salts would then have the formulæ $(C_2H_4)_2S_2(C_2H_5)Cl,PtCl_4$ and $[(C_2H_4)_2S_2]_2(C_2H_4)Cl_2,2PtCl_4$. The following table gives a comparison of the percentage composition required by the first of these with that required by Dehn's theory and with the numbers deduced from his analysis:—

	Calculated for $(C_2H_4)_2S_2(C_2H_5)Cl,PtCl_4$.	Found by Dehn.	Calculated for $(C_2H_4)(C_2H_5)_2SCl_2,PtCl_4$.
C......	13·81	14·17	13·69
H......	2·49	2·66	2·66
S......	12·27	—	6·08
Pt.....	37·39	37·29 and 37·24	37·07
Cl.....	34·04	—	40·50
	100·00		100·00

Though the differences are comparatively small, they are significant; and they do not favour Dehn's formula. Had he estimated either sulphur or chlorine, it is obvious that he would have come to a different conclusion.

The evidence as to the constitution of the other sulphine salt, or indeed of its existence, is so slight that it seems almost superfluous to suggest that it was most probably $\{(C_2H_4)_2S_2\}_2(C_2H_4)Cl_2,2PtCl_4$. This requires 38·50 per cent. of platinum: Dehn found in his first fractions 39·13 and 38·39 per cent. But there is reason to believe, from the following experiment, that the corresponding bromide, as well as the salt $(C_2H_4)_2S_2(C_2H_5)Br$, must have been produced in Dehn's reaction, though in small quantity.

Two sealed tubes were prepared, the one containing diethylene disulphide with excess of ethyl bromide and the other diethylene disulphide with excess of ethylene bromide. After being heated for several hours at a temperature of 125—150°, they were cooled and opened. In each case, free hydrobromic acid and disagreeable volatile sulphur compounds were found to have been formed, but the bulk of the disulphide was unaffected. By extraction with warm water, however, small quantities of a sulphine bromide were obtained from each tube; and these possessed the following characteristic properties, a comparison of which with those of the salts of diethylenesulphide-methyl-sulphine removes any possible doubt as to their true nature.

(1.) They both undergo partial decomposition when their solutions are evaporated to dryness, a white insoluble substance being produced. The decomposition occurs to a greater extent than in the case of the corresponding methyl salts.

(2.) They are both decomposed by heating with alkalis: a sudden turbidity occurs, due to the separation of a white flocculent solid, and a volatile sulphur compound is evolved having a strong and peculiar odour. This odour is different in the two cases; for, whilst that derived from the ethylsulphine exactly resembles the smell of the oil $C_{12}H_{24}S_5$ (p. 247), that from the ethylene compound is of a more pleasant character.

(3.) With recently precipitated silver oxide, they give alkaline solutions, which, on the addition of hydrochloric acid, and, after warming, of platinic chloride, yield insoluble yellow amorphous precipitates.

These facts and the considerations already adduced seem to justify the following equations, III and IV, being written in lieu of Dehn's. The whole scheme for the reaction becomes—

$$\text{I. } 2C_2H_4Br_2 + 2(C_{25}H)_2S = (C_2H_4)_2S_2 + 4C_2H_5Br.$$
$$\text{II. } C_2H_5Br + (C_2H_5)_2S = (C_2H_5)_3SBr.$$
$$\text{III. } C_2H_5Br + (C_2H_4)_2S_2 = (C_2H_4)_2S_2(C_2H_5)Br.$$
$$\text{IV. } C_2H_4Br_2 + 2(C_2H_4)_2S_2 = [(C_2H_4)_2S_2]_2(C_2H_4)Br_2.$$

It is probable that the iodides of ethyl and ethylene would combine with diethylene disulphide much more readily and completely than the bromides. If this be so, the products may repay an investigation, more particularly the ethylene one. I propose therefore to continue my experiments.

XXVIII.—*Certain Aromatic Cyanates and Carbamates.*

By H. Lloyd Snape, B.Sc.

Continuing some experiments on phenyl cyanate already reported (*Chem. Soc. Trans.*, 1885, 770), I examined its action on pyridine. No reaction takes place in the cold, when these liquids are mixed in about molecular proportions, but on boiling, and then allowing the mixture to remain in a vessel closed by a drying tube containing calcium chloride, beautiful crystals are formed. These are only sparingly soluble in ether, but somewhat more soluble in alcohol; on recrystallisation from the latter, small quadratic plates are obtained melting at 175°. This melting point, the form of the crystals, the relation to solvents, and the fact that a large proportion of the pyridine remains unchanged, suggested the probability that the phenyl cyanate had condensed in the presence of this base to diphenyl dicyanate. On analysis this proved to be the case.

	Calculated for $C_{12}H_{10}N_2O$ (*i.e.*, $C_5H_5N + C_6H_5NCO$).	Calculated for $C_{14}H_{10}N_2O_2$.	Found.
N	14·14	11·76	12·27

Many years ago Hofmann showed (*Ann.*, Suppl. 1, 57; *Ber.*, 3, 765, and 4, 246) that a small quantity of triethylphosphine brought

about this change; but pyridine is more suitable as being much cheaper and more readily obtained.

The account of the preparation of a phenylene dicyanate by Gattermann and Wrampelmeyer (*Ber.*, **18**, 2604), by a method analogous to that by which Hentschel obtained phenyl cyanate (*Ber.*, **17**, 1284), suggested to me that other dicyanates might be prepared in a similar manner, and I could then examine their action upon alcohols, as I had previously done with phenyl cyanate. The action of phosgene on benzidine was first investigated.

Diphenylene Diisocyanate, $CO\!:\!N\cdot C_6H_4\cdot C_6H_4\cdot N\!:\!CO$.

A current of phosgene was passed over well-dried benzidine hydrochloride contained in a fractional distillation flask, heated in a paraffin-bath at 230° to 250°. A small quantity of a colourless oil passed over, and solidified in the delivery tube leading from the flask. In later experiments it was found preferable, as giving a better yield, to conduct phosgene for about two hours over the salt heated in benzoic acid vapour (b. p. 250°), finally distilling over the cyanate, still in an atmosphere of phosgene, by means of a bath of diphenylamine vapour (b. p. 310°). Probably a substituted carbamide is first formed, as with aniline; and a higher temperature is required to completely decompose this and to drive off the cyanate. The two phases of reaction would, according to this hypothesis, be represented by the following equations:—

$$(1.)\ NH_2\cdot C_6H_4\cdot C_6H_4\cdot NH_2 + COCl_2 = 2HCl + CO{<}{\substack{NH\cdot C_6H_4\\ NH\cdot C_6H_4}}{>}.$$

$$(2.)\ CO{<}{\substack{NH\cdot C_6H_4\\ NH\cdot C_6H_4}}{>} + COCl_2 = CO\!:\!N\cdot C_6H_4\cdot N\!:\!CO + 2HCl.$$

The distillate was almost pure and solidified in splendid long needles. These were quite insoluble in cold water and in hydrochloric acid, and therefore did not contain any of the original salt or free benzidine. On the other hand, traces of hydrochloric acid adhered somewhat persistently to the cyanate. On heating it, the greater part melted and then sublimed, but a portion was always decomposed. The vapour had the peculiar odour of phenyl cyanate. It softened a little under 100°, and the purest looking specimen I obtained melted at 122°. Another portion after sublimation, and in external appearance almost as pure, melted at 116° to 120°. The difficulty of obtaining it *absolutely* free from hydrochloric acid made it difficult to fix within a few degrees the melting point of the pure substance. It was soluble in ether. Analysis:—

	Calculated for $C_{14}H_8N_2O_2$.	Found. I.	Found. II.
N	11·86	11·37	11·35

As was to be expected, this cyanate, like phenyl cyanate and phenylene dicyanate, yielded carbamates with alcohol and phenol.

Diphenylene-diurethane or Diethyl Diphenylenedicarbamate,
$COOC_2H_5{\cdot}NH{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}NH{\cdot}COOC_2H_5$.

A portion of the above cyanate was dissolved in just as much boiling alcohol as was necessary, the boiling continued for a few minutes, and then the solution was allowed to remain undisturbed to cool. The crystalline deposit was almost pure, and, when recrystallised from alcohol after previous boiling with animal charcoal, separated in beautiful feathers. These crystals melted about 226°, but it is somewhat difficult to determine *exactly* the melting point, as a decomposition sets in at about the same temperature.

	Calculated for $C_{18}H_{20}N_2O_4$.	Found.
N	8·54	8·66

The constitution of this compound was further confirmed by preparing it from ethyl chlorocarbonate and benzidine. Benzidine was treated with the ethyl chlorocarbonate—an excess of the latter being present—in a vessel supplied with a reflux condenser, and heated for about 20 minutes in an oil-bath at 130°. On merely mixing, a considerable amount of heat was developed, and the reaction then mainly took place. After distilling off the excess of ethyl chlorocarbonate, the remaining brownish-white solid was washed well with water, and recrystallised from alcohol. The same peculiar feathery crystals were obtained. These melted at about 230°. The slight difference in the melting point is explained by the already-mentioned difficulty of determination. The reaction in this case is as follows:—

$$2(NH_2{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}NH_2)+2(Cl{\cdot}CO{\cdot}OC_2H_5)=(NH_2{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}NH_2,2HCl) + (COOC_2H_5{\cdot}NH{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}NH{\cdot}COOC_2H_5).$$

The benzidine hydrochloride which is simultaneously formed is separated by its solubility in water.

Diphenyl Diphenylenedicarbamate,
$COOC_6H_5{\cdot}NH{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}NH{\cdot}COOC_6H_5$.

Diphenyl dicyanate was heated with a slight excess of phenol in an oil-bath at 140°. These substances at first melted, and afterwards

solidified again, showing the formation of a compound of higher melting point than either. This was found to be but sparingly soluble in most ordinary solvents, such as alcohol, ether, benzene, &c. After previously washing well with ether to remove phenol, it was recrystallised from glacial acetic acid, as this solvent seemed to be the best. A large quantity of acetic acid was required. After a second recrystallisation, the carbamate was obtained in beautiful crystalline tables. These were washed with ether many times to remove acetic acid, dried, and finally submitted to analysis.

	Calculated for $C_{26}H_{20}N_2O_4$.	Found.
N	6·60	6·84

The melting point was about 240°, but was difficult to determine with precision, as the substance decomposes with evolution of gas at about the same temperature.

Metatoluylenediamine, $CH_3\cdot C_6H_3(NH_2)_2$, was next treated with phosgene: *metatoluylene diisocyanate*, $C_6H_3(CH_3)(NCO)_2 = [1:2:4]$, was thus obtained. Toluylenediamine hydrochloride was treated with phosgene in an exactly similar manner to that described for obtaining diphenyl dicyanate, viz., successively in benzoic acid and diphenylamine vapour-baths. The toluylene dicyanate passed over as a pale-yellow liquid, which solidified to groups of needles almost perfectly white. The needles were smaller than those of diphenylene dicyanate. The compound as thus collected was almost pure, although contaminated to a slight extent with hydrochloric acid, which could not be readily removed. The melting point was 94°. On distilling the substance, it lost hydrochloric acid, and though it passed over mainly unchanged, was in part decomposed, the melting point being considerably lowered.

	Calculated for $C_9H_6N_2O_2$.	Found.
N	16·09	15·56

It was soluble in ether, and possessed the strong and unpleasant odour of phenyl cyanate, especially noticeable on gently heating.

Thus, in all its properties this compound corresponds to, and is evidently identical with, that described by Lussi (*Ber.*, **7**, 1263, and **8**, 291). He obtained in the first place the corresponding urethane, by treating toluylenediamine with ethyl chlorocarbonate, and then distilled this urethane with phosphoric anhydride. In order to confirm the identity, a portion of the cyanate, as prepared by me, was boiled with alcohol, and on allowing it to stand, white silky needles separated. These were soluble in ether, and melted at 135°. These

properties agree with the description of the urethane given by Lassi. For complete control, a small quantity was prepared as described by him from ethyl chlorocarbonate and metatoluylenediamine, recrystallising the product from alcohol. I thus obtained exactly similar lustrous needles, melting at 135°; they gave the following results on analysis:—

	Calculated for $C_{13}H_{18}N_2O_4$.	Found.
N	10·53	10·64

Lussi states the melting point to be 137°. I converted another portion of the cyanate into the phenol carbamate.

Diphenyl-toluylene Dicarbamate, $C_6H_3(CH_3)(NH{\cdot}COOC_6H_5)_2 = [1:2:4]$.

Metatoluylene isocyanate, as prepared above, was heated with an excess of phenol in an oil-bath at from 130° to 150° for half an hour. A gelatinous mass was obtained, which when boiled with ether to remove phenol, became changed into a gray powder. This was recrystallised from hot glacial acetic acid in which it readily dissolved. Clusters of white needles separated on cooling. These were collected, well washed with ether to remove excess of acetic acid, and dried at 105°. The compound was slightly soluble in alcohol and ether and melted at 147·5°.

	Calculated for $C_{21}H_{18}N_2O_4$.	Found.
N	7·73	7·87

The next attempt which was made was to treat *orthotoluylenediamine with phosgene.* I did not succeed, however, in obtaining any cyanate in this case. It was recently noticed by Gattermann and Wrampelmeyer, that whilst para- and meta-phenylenediamine are each converted respectively by phosgene into the corresponding cyanates, orthophenylenediamine is not. Their experience and my own may probably be explained by the suggestion that the orthodiamine is first converted into an ortho-substituted carbamide, and that then the NH-groups are held so firmly by the CO-group as not to permit of further decomposition by phosgene. Thus, in the above case, the reaction is probably—

$$C_6H_3(CH_3)<^{NH_2}_{NH_2} + COCl_2 = 2HCl + C_6H_3(CH_3)<^{NH}_{NH}>CO.$$

But the compound refuses to be further converted into the corresponding dicyanate, as is the case when the NH-groups are attached to carbon-atoms further apart in the benzene-ring.

The corresponding urethanes which would result from the action of alcohol on these cyanates, can, however, be prepared by the action of ethyl chlorocarbonate on the amines.

Orthophenylene-diurethane, $C_6H_4(NH{\cdot}COOC_2H_5)_2 = [1:2]$, was prepared in this way. Orthophenylenediamine was heated with an excess of ethyl chlorocarbonate at 130°, the unaltered ethyl chlorocarbonate distilled off, and the residue washed with water and hydrochloric acid. By recrystallisation from alcohol, after previously boiling the solution with charcoal, lustrous needles melting at 88° were obtained. The dried compound was submitted to analysis.

	Calculated for $C_{12}H_{16}N_2O_4$.	Found.
N	11·11	11·31

Orthotoluylenediamine also reacted *with ethyl chlorocarbonate*, and crystals separated from the alcoholic extract of the product. I have not as yet purified and analysed this compound.

Lastly *phenylhydrazine* was treated with *phosgene*. The latter was conducted over phenylhydrazine hydrochloride, heated at 220° to 230° in a paraffin-bath. Towards the close of the operation, the temperature was allowed to rise to 250°. A pale-brown oil distilled over, and solidified on cooling to a pasty mass. The product of the reaction possessed the powerful odour of phenyl cyanate, and the vapour strongly attacked the eyes. On heating it in a fractional distillation flask, hydrogen chloride was evolved, and a portion sublimed in splendid long needles. Pressed out on porcelain, it gradually but entirely sank into the plate. Instead of the reaction taking place as I hoped, according to the equation—

$$C_6H_5{\cdot}NH{\cdot}NH_2 + COCl_2 = C_6H_5{\cdot}NH{\cdot}NCO + 2HCl,$$

a solid combination of phenyl cyanate and hydrochloric acid had been formed. That phenyl cyanate has the property of dissolving large quantities of hydrogen chloride to form a solid mass is mentioned by Hentschel (*Ber.*, **17**, 1285, and **18**, 1178). That this curious combination had taken place in this case was shown by the evolution of hydrogen chloride on heating the product; by the continued characteristic and unpleasant odour of phenyl cyanate, which was so unbearable that it could not be worked with for longer than a few minutes consecutively, and lastly by its conversion into carbanilide. This was effected by simply boiling with water in a flask provided with a reflux condenser until the odour of phenyl cyanate had disappeared. The crystalline needles thus formed, after recrystallisation from alcohol, were shown to have the same melting point and percentage of nitrogen as carbanilide. Phenyl cyanate, as is well known, is readily

converted into carbanilide by the action of water. The experiment did not allow me to determine whether phenylhydrazine was at first decomposed, yielding aniline, which, together with phosgene gave phenyl cyanate, or whether the cyanate, $C_6H_5 \cdot NH \cdot NCO$, I had expected to obtain was first formed, but then decomposed, yielding phenyl cyanate.

I have much pleasure in taking this opportunity to express my best thanks to Dr. Gattermann, for valuable counsel afforded by him to me during the course of the work above described.

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XXIX.—*The Influence of Temperature on the Heat of Chemical Combination.*

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Our knowledge of the influence which temperature exerts on the heat of chemical combination is at present of the most rudimentary character. It has been established as one of the fundamental principles of thermochemistry that the total heat evolved in the combination of two substances at different temperatures, together with that necessary to reduce the systems in the two cases to the same initial and final temperatures, is a constant quantity—that where Q and Q′ represent the actual heat evolved during the combination of A with B at T and T′, we shall have—

$$Q - C_{AB}(T' - T) = Q' - (C_A + C_B)(T' - T),$$

C_A, C_B, and C_{AB} being the specific heats of A, B, and the compound which they form, respectively. Where the specific heat of the compound is equal to the sum of those of its components, the heat which these develop in combining will be a constant quantity independent of temperature. The labours of Kopp have shown that such a condition exists to a certain extent in the case of most solids, but we are still in ignorance as to whether it is absolutely or only approximately true, whether those variations which have in many cases been observed in the specific heats of solids are regular in their nature, whether, in fine, the compound AB at T is in every respect the same substance as AB at T′.

The present investigation shows that this is not the case. It will appear that the relation between the constituent portions of the molecule of a complex solid undergoes a series of modifications as the temperature changes, the result of which is that the variations exhibited in the heat of combination, and consequently in the specific heat also, being conditioned by a different order of circumstances at different temperatures, exhibit irregularities of a very marked character.

As no methods have yet been devised for obtaining very accurate measurements of specific heats through small, or indeed through considerable ranges of temperature, the heat of combination appeared to be the only available means of investigating the subject; in order, however, to invest the determinations of it with a degree of accuracy which would promise any chance of success, it was necessary to confine them within the limits of ordinary atmospheric temperatures, a small range of 25° C. only being thus available. Substances which would be most likely to exhibit any variation in the heat of their formation within these narrow limits would be those in which the energy of combination was small. Hydrated salts afford many instances of such a nature, and, consequently, they were chosen as the subjects of this investigation; the heat of hydration presents, moreover, one other material recommendation for the present purpose, in that the number of operations necessary for a determination of it is very limited, and the nature of these is very simple.

Whatever may be the complexity of the reactions occurring when a salt is dissolved in water, it is generally accepted that the difference between its heat of dissolution in the anhydrous and hydrated state gives the heat of combination of the salt with its water of crystallisation,* provided we first subtract from the second of the above-named quantities the heat absorbed in the conversion of the solid water present into liquid water, for every fact which bears on the question supports the view that in a solid hydrated salt the water is present as a solid, and in the solution of such a salt as a liquid.

The heat of fusion of ice at temperatures other than 0° never having been determined experimentally, it must be calculated by means of the specific heats of water and ice; the latter of these has also never been determined for temperatures above 0°, and, consequently, some doubt must be felt as to the correctness of the values calculated for the heat of fusion. The present experiments themselves, however, will be found to afford considerable evidence as to the accuracy of these calculated values, and, moreover, any error in them will not affect the main conclusions drawn from this work,

* This can only be so if the heat of combination of the various atoms composing the salt molecule is unaffected by the combination of that molecule with the water.

inasmuch as such errors would affect the inclination of the curves only, and not their nature. The latent heat of fusion of 1 mol., or 17·96 grams, of water, l_m, has been calculated from the equation—

$$l_m = (1423 \cdot 33 + (c - c')T) \text{ cal.},$$

in which the specific heat of water,

$$c = 17 \cdot 96 + 0 \cdot 00072T + 0 \cdot 0000162T^2,$$

and the specific heat of ice, $c' = 9 \cdot 052 + 0 \cdot 0185T$. The various values of l_m, which is of course a negative quantity, are represented in Plate VII, and it will be seen that, for the purposes of the present communication, this is practically a straight line.

The heat of combination of a salt with its water of crystallisation, both being in the solid state, will be given by the equation—

$$Q = M_A - (M_H + xl_m),$$

in which M_A and M_H represent the observed heat of dissolution of anhydrous and hydrated salt, and x the number of molecules of water which the latter contains. If, as has hitherto been assumed, the specific heat of a hydrated salt is equal to the sum of that of the anhydrous salt and the water (reckoned as solid water), the value of Q will be a constant quantity, independent of temperature.

The more important conclusions arrived at in this paper are based on differences so small as to be nearly on a par with those attributable to experimental error; it will, therefore, be necessary to enter considerably into detail to show that they can by no means be attributed to this source.

Apparatus and Method Employed.

The apparatus employed was Berthelot's open calorimeter, and full details as to the method of operation adopted in this research will be found in *Phil. Mag.*, 1886, **21**, 324. It will be sufficient to mention here that, except in some of the earlier experiments, and in some of those at very low temperatures, the temperature of the air was kept constant within about 0·2° of the initial temperature of the calorimetric water. This precaution, which naturally rendered the experiments very tedious, was necessary, in order to reduce the errors inherent in the determination of the rate of cooling to a minimum, and it also obviated any important correction having to be applied on account of the temperature of the salt before dissolution not being identical with that of the water in which it was dissolved.

The rate of cooling (or heating) was determined in every single experiment, and the necessary correction applied, for it was ascertained

that not in one case out of a hundred did the salt dissolve in a space of time sufficiently short to render such a correction superfluous.

The general method of procedure was modified in the case of hydrated sodium sulphate only. The adhesive nature of this salt rendered it impossible to shake it out of the weighing-tube into the calorimeter without causing an inordinate amount of splashing; the following device was, consequently, adopted in one series of experiments (those with sample No. 3095). The salt was weighed out into a very short wide test-tube, of which the water equivalent was known, and the tube with its contents plunged bodily into the water; a platinum wire fused into the bottom of the tube served as a means of holding the tube inverted till its contents had fallen out. It was found, however, that the presence of these tubes in the calorimeter interfered with the agitation of the liquid to such an extent that, at low temperatures, a very long time elapsed before all the salt dissolved. In the experiments with other samples, therefore, the salt was weighed out into the ordinary test-tubes on feet, but instead of being shaken out into the water, it was shaken out on to the flat disc which formed the end of the agitator, and which for that purpose was momentarily raised till flush with the level of the water. All splashing was thus avoided. The raising of the pounder was repeated in each interval, during which the rate of cooling was measured, so that any error due to evaporation from its surface during the process might be allowed for; no additional error appears to have been caused by this operation, as the average variation of duplicate experiments in this series is not greater than that in other cases.

Thermometers Employed.

Two calorimetric thermometers were at first employed, No. 55,083, with a range of 1—16° C., and No. 55,081, with a range of 10—25°; subsequently another instrument, ranging from 5—21°, was used (No. 56,916), and in a few experiments No. 55,080, a fellow instrument to No. 55,081, as well as No. 55,084, with a range of 0—26°. They were divided into about 38 arbitrary degrees, each of which were subdivided into tenths, these subdivisions being 1·2 mm. apart, and each equivalent to about 0·038° C. In reading them, a pocket lens was employed, and the fractional portions estimated to the twentieth of the marked divisions, one estimation unit, therefore, representing 0·002°. With No. 55,084, these quantities must be doubled, as the range in its case is twice as great as with the others.

These calorimetric thermometers were originally standardised by comparison with a natural standard, but as the work progressed it became apparent that this method was insufficient to afford

the amount of accuracy required, since a small error in the reading of the standard would cause a very appreciable want of concordance in the various instruments. The following expedient was therefore adopted:—All the thermometers were compared with No. 55,084, the range of which embraced those of all the others, and which was thus converted into an "intermediate standard;" as this instrument is about three and a half times as delicate as the natural standard, a corresponding increase in the concordance of the calorimetric instruments was thus attained. It is true that this "intermediate standard" itself had to be standardised by comparison with the natural standard, but any error made in this operation would affect all the calorimetric instruments to the same extent, and would not impair their concordance *inter se*, which was here the consideration of most importance. The results thus obtained were further modified by comparing the calorimetric instruments with each other, this being effected by comparison with No. 56,216, the scale of which overlapped that of all the others to a considerable extent, twelve or more comparisons at different points being made with each instrument, a fall or rise of about 170 mm. (2·3°) being taken in each observation.

At the same time that this re-standardising was effected, all the instruments were calibrated afresh, and all the several hundred experiments which had been completed were recalculated. Some details as to these calibrations and standardisations will be found in the *Phil. Mag.*, 1886, **21**, 180.

In spite of the very great pains which were taken to produce an absolute concordanee between the various thermometers, the results were not altogether satisfactory; indeed a certain regularity which appeared in the differences of the results obtained with different instruments, seemed to indicate the existence of some unknown imperfection inherent in the nature of mercurial thermometers, which prevented the attainment of such concordance throughout the scales.

A device was consequently adopted, by means of which not only the same thermometer, but also the same part of the thermometer, was used in every experiment, whatever the temperature might be. This was effected by removing the requisite amount of mercury into the upper chamber of the instrument by the application of heat, thus adjusting its reading to any particular temperature, and rendering two experiments at different temperatures as comparable with each other as if they had been performed at the same temperature: in fact, for the purposes of the present investigation, the errors of calibration and standardisation were thus obviated entirely.* At the same time, the delicacy of the instruments was increased six- or seven-fold; in two of them (Nos. 62,839 and 63,616) the total range of about 600 mm.

* A similar device has, I believe, been used by Crafts.

represented 3·6° and 3·86° respectively, each estimation unit (0·05 mm. in this case) being equivalent to 0·0003° only. A full description of these thermometers, together with some peculiarities which they exhibit, and the manner in which these must be guarded against, has been given in the *Phil. Mag.*, 1886, **21**, 330.

Quantities Used.

The relative proportions of salt and water used in all these experiments was 1 mol. of a single salt to 400—420 mols. of water, the actual quantities being $\frac{3}{40}$ths of a gram-molecule to 600 c.c.

Chemists have generally preferred to take proportions of water not exceeding $200H_2O$, but though such a proportion gives twice the temperature disturbance, the larger quantity, $400H_2O$, would appear to offer greater facilities for very accurate measurements in most cases. The estimation of the rate of cooling is certainly that part of a determination which admits of the largest error, and the employment of $200H_2O$ in these experiments would have increased the rate of cooling beyond the limits within which that rate is practically constant in the case of three of the salts, while in all the cases in which anhydrous salts were dealt with, the larger proportion of salt would have required twice the time pounding and stirring to have effected its dissolution, and would thus have doubled the correction necessary for cooling. Moreover, with the instruments employed, a rise or fall of as much as 5°, which would have occurred in some cases had $200H_2O$ been used, would have limited very materially the range of temperature available for the series of experiments, and would have rendered it impossible to use such delicate thermometers as the last two described.

Another inducement for taking the larger proportion of water will be mentioned when the calculation of results is discussed.

With double salts, the proportion of salt was only one-half of that used in the other cases.

Experimental Error.

As the question of experimental error in these experiments has been fully discussed in the *Phil. Mag.*, 1886, **21**, 324, it will be necessary to mention here the general results only.

One estimation unit (0·06 mm.), in the case of the less delicate thermometers, represents 16 cal. in the molecular heat of dissolution of a single salt, while with the two more delicate ones it (0·05 mm.) represents 2·5 cal.

The experimental error where the former were used was found to be ± 18·86 cal. for every single experiment; of this ± 5·56 cal. is

due to errors in the calibration and standardisation of the instruments, leaving $\pm$ 13·3 cal. as the error of each experiment, when duplicate determinations at the *same* temperature, and performed with the *same* instruments, are compared. Of this error, $\pm$ 5·71 cal. have been traced to error in reading the instruments, and $\pm$ 7·59 cal. to error in manipulation. In cases where two thermometers were used simultaneously in the calorimeter, the manipulation error is increased to $\pm$ 9·53.

With the two very delicate instruments, the total probable error of each experiment was only $\pm$ 7·42 cal., this being the error when comparing experiments performed, not only at the same temperatures, but at different temperatures also.

In the case of the double salts, all the above numbers become doubled.

Calculation of Results.

The salt before its introduction into the calorimeter being at very nearly the same temperature as the water, the correction due to the "salt temperature" was generally very small, rarely amounting to one estimation figure of the thermometer. The specific heats from which any such correction was calculated were taken as follows:—

$Na_2SO_4,10H_2O$, 0·320; Na_2SO_4, 0·229; K_2SO_4, 0·190; Li_2SO_4, 0·200; $CuSO_4,5H_2O$, 0·300; $CuSO_4$, 0·135; $MgSO_4,7H_2O$, 0·380; $MgSO_4$, 0·222; $CuSO_4,K_2SO_4,6H_2O$, 0·260; $CuSO_4,K_2SO_4$, 0·168; $MgSO_4,K_2SO_4,6H_2O$, 0·264; $MgSO_4,K_2SO_4$, 0·170.

Having applied this correction, as well as that due to cooling (or heating) during the dissolution, the heat evolved was calculated from the initial and final temperatures thus obtained, according to the simplified method adopted by Berthelot (*Méc. Chim.*, **1**, 190), which consists in reckoning the number of cubic centimetres of water originally taken as so many grams with a specific heat of 1, and neglecting the salt present. It is true that the specific heat of solutions containing 1 mol. of the salt to $200H_2O$ has been determined for some of the substances here dealt with (Marignac, *Arch. des Sc. de la Bibl. de Genève*, 1876), and that the employment of solutions of that strength would have allowed of the adoption of a more accurate method of calculation in such cases; but even in the few instances where it would have been possible, its application would have been limited to the experiments at one temperature only, since the data for calculating the specific heats at any temperature between 0° and 25° are entirely wanting.

Berthelot shows that in many cases his method introduces but ve[ry] trifling errors, and gives far more accurate results than are obtain[ed]

by assuming the specific heat of dilute solutions to be unity. With solutions as dilute even as those containing $200H_2O$, it is liable, however, in some cases to lead to serious errors, taking for instance copper sulphate. 23·8 grams of the anhydrous salt would be dissolved in 602 05 c.c.* (weighing 600·5 grams) at 24°; the specific heat of such a solution at this temperature is 0·95, and hence its water equivalent will be $(600·5 + 23·8)0·95$, or 593·1 grams, whereas according to Berthelot's method, it would be taken as 602·05 grams, thus causing an error of $\frac{1}{70}$th. This error, however, is greatly reduced by using more dilute solutions. From Marignac's work on the specific heat of saline solutions (*loc. sup. cit.*), we may conclude that the specific heat of solutions of various sulphates differ from each other to a smaller extent the more dilute they are; that with $400H_2O$ their specific heat will probably be very near 0·98°, and that a rise of temperature of 1° will cause an increase of approximately 0·0001 in this specific heat. Taking now two experiments with copper sulphate with $400H_2O$ at 24° and 4° respectively. At 24°, the water taken would have measured 602·05 c.c., and weighed 600·50 grams. The weight of salt taken would be 11·9 grams. The water equivalent of the solution would be $(600·5 + 11·9)0·98 = 600·05$ grams, whereas it would have been taken as 602·05 grams, the error, therefore, being $\frac{1}{300}$th. At 4° the water taken would be 601·74 c.c., weighing 601·74 grams, and the true water equivalent $(601·74 + 11·9)0·978 = 600·14$, that taken 601·74, the error being $\frac{0·8}{300}$th. Such errors (and I have taken an instance where it would appear to be larger than in most cases) would often be within the limits of the experimental errors, and, as will be seen, the conclusions drawn in this communication do not depend on the absolute accuracy of the numbers given, but on the relative accuracy of experiments with the same salt at different temperatures (the error in comparing together the above experiments would be only $(\frac{1}{300} - \frac{0·8}{300} =)\frac{1}{1500}$th), and on a comparison of the heat of dissolution of the anhydrous and hydrated salts at the same temperature. All the experimental data, however, will be given in full, so that in the event of future work completing our knowledge of the specific heats of saline solutions, these results may be recalculated in a more correct manner.

Preparation of the Salts.

The method generally adopted in preparing the hydrated salts consisted in recrystallising them very carefully two or three times,

* I take the volumes which would actually have been used in the present experiments; these are the volumes delivered by the same glass vessel at the various temperatures. No difference would be made in the present calculations were the *same* volumes taken at every one of the temperatures.

powdering the crystals finely, and washing them with water. This powdering and washing is very necessary in the case of all sulphates containing copper, or any allied metal, since, owing to the dissociation of the salt in solution, any mother-liquor adhering to the crystals will be acid, and this will cause serious errors to arise in the colorimetric determinations. It is also preferable in such cases not to boil the solutions of the salt, since a high temperature greatly increases the amount of this dissociation.

The hydrated salts were invariably sifted, sometimes through a silk sieve.

Considerable difficulty was at first experienced in prepaing these salts with exactly the theoretical amount of water, owing to efflorescence. The most satisfactory results were obtained by determining the percentage of water present in the crystallised salt which had been imperfectly dried, and then allowing it to lose whatever excess of water it was found to contain, by exposing weighed quantities of it to the air with constant stirring. It was ascertained that even a large quantity of a salt which retained excess of moisture could, by sifting and mixing, be obtained sufficiently homogeneous throughout to render such a method trustworthy.

To take one instance out of many, a sample of hydrated sodium sulphate weighing 1 kilo. gave on analysis 56·612, 56·611, and 56·596 per cent. of water, numbers which are very closely concordant, although the sample contained a considerable amount of adhering moisture, the theoretical percentage for $Na_2SO_4,10H_2O$ being only 55·88.

The most accurate and indeed the only satisfactory means of analysing most of the sulphates here dealt with, was found to be a determination of the percentage of water present in them, using very large quantities for each analysis. This method has already been discussed in a previous paper (Trans., 1885, 100), and the analytical results will not be given in the present communication, since, unless the water percentages were found to correspond to the theoretical amount within experimental error (within about 0·03 per cent.), the preparation was rejected.

In the case of a hydrated salt, such as sodium sulphate which parts with its water of crystallisation very easily, it was found necessary to prevent the salt from caking in the bottle in which it was preserved, by constant agitation, for if it cakes some of the water from the crystals in one part of the bottle distils into another part which happens to be slightly cooler, so that the sample is no longer homogeneous. A whole series of experiments was spoilt by neglecting this precaution.

It was found best to preserve the anhydrous salts in small bottles

or sealed tubes, each containing sufficient for only two or three determinations, so that exposure to the air might be avoided as much as possible; in order, however, to make sure that the contents of each bottle or tube were precisely the same as regards their state of purity, it was necessary to put the whole of the sample into a big bottle immediately after its preparation, keep it there with continual shaking for several days, and then after heating it in the bottle itself to a temperature considerably above 100°, to transfer it to the smaller vessels.

The experiments were so arranged that different determinations at the same temperature were made after long intervals of time, so that any alteration in the salt, whether of a molecular or of accidental nature, might be detected. In no case was any such molecular alteration observed, and only in one instance (with a sample of copper sulphate) was any difference detected, and that was due to accident.

Specimens Used.

The following are the preparations which were used in the various experiments. For the sake of reference, I have retained the numbers by which they were distinguished when prepared.

Hydrated Magnesium Sulphate, $MgSO_4,7H_2O = 245{\cdot}48$.—This salt when pure neither effloresces nor deliquesces on exposure to air; its preparation, therefore, is very easy. Three different specimens, Nos. 2688, 2756, and 3417, were used in the majority of the experiments, as well as three others in a few cases.

Anhydrous Magnesium Sulphate, $MgSO_4 = 119{\cdot}76$.—Samples 2718 and 2754 were prepared by heating the salt in small quantities in a platinum dish below a red heat. No. 3092 was dehydrated at a temperature of 250° only.

Hydrated Potassium Magnesium Sulphate, $MgK_2(SO_4)_2,6H_2O = 401{\cdot}4$.—Prepared by cooling a hot saturated solution of the component sulphates. The details of its preparation in a state of purity are given in this vol., p. 8.

Four different samples were used.

Anhydrous Potassium Magnesium Sulphate, α-$MgK_2(SO_4)_2 = 293{\cdot}64$.—Five preparations of this salt were made. The difficulty of obtaining it in the anhydrous condition without inducing a change which converts it into a second modification necessitated the employment of samples retaining small quantities of water (except with No. 3039) for which a correction had to be applied. No. 3432 had been somewhat overheated, and gave numbers uniformly 1113 cal. lower than the other samples. This amount was added to experiments with it for convenience in deducing a curve. The peculiarities of this salt,

and those of the corresponding copper compound, formed the subject matter of a communication to the Society, and full details as to most of the specimens here used will be found in this vol., p. 1 *et seq.*

Hydrated Copper Sulphate, $CuSO_4,5H_2O$ = 248·64.—One specimen only of this salt was used, No. 2736.

Anhydrous Copper Sulphate, $CuSO_4$ = 158·84.—Eight different preparations were used. The first one, No. 2729, having been kept in one bottle, was found to have accidentally absorbed a certain amount of moisture, which rendered the numbers yielded by it in the later determinations uniformly 160 cal. lower than those given in the earlier ones. This amount has consequently been added to the later experiments with it, as indicated in Table III. Nos. 3094 and 3401 were preserved in small bottles, and the remaining specimens in sealed tubes. All the specimens were prepared at a temperature between 200° and 250°.

Hydrated Potassium Copper Sulphate, $CuK_2(SO_4)_2,6H_2O$ = 440·78.—Two specimens of this salt, prepared in the same manner as the corresponding magnesium compound, were used; one of them, however, in two experiments only.

Anhydrous Potassium Copper Sulphate, α-$CuK_2(SO_4)_2$ = 333·02.—The four different specimens used were prepared by dehydrating the crystallised salt at temperatures between 115° and 130° (*vide supra*).

Hydrated Sodium Sulphate, $Na_2SO_4,10H_2O$ = 321·41.—Two different specimens, Nos. 3095 and 3418, were prepared from totally different samples of the commercially pure salt.

Anhydrous Sodium Sulphate, Na_2SO_4 = 141·81.—Seven preparations of this salt were examined. No. 3036, prepared by drying the effloresced hydrated salt over sulphuric acid. Nos. 2775 and 3052, samples dried at 100°. No. 3081, dried at 150°. These were all obtained from the same lot of the hydrated salt.

Owing to the excessive degree in which this salt cakes, it was impossible to make any accurate determinations with these samples below 10°. It was found, however, that the anhydrous sulphate precipitated by heating a saturated solution of the salt above 3[illegible] the dissolved without difficulty, and evolved the same amount of hea[illegible] the non-crystalline specimens prepared by efflorescence (see Tr[illegible] 1884, 689). Three samples (Nos. 3098, 3407, and 3604) were prepared in this manner from different lots of the hydrated salt.

Potassium Sulphate, K_2SO_4 = 173·88.—Four different preparations were made, the finely-powdered salt being sifted through s[illegible]ilk, and then heated for many hours at 200—250°. These specimens did not yield absolutely concordant numbers for their heat of dissolution, due no doubt to the temperature at which they were prepared not being exactly the same (see Trans., 1885, 98). The various results were

reduced to uniformity with those of No. 3603, by adding 18 cal. to those with 2725, — 38 cal. to those with 3428, and — 63 cal. to those with 3613.

Anhydrous Lithium Sulphate, $Li_2SO_4 = 109{\cdot}84$.—The experiments with this salt do not claim the same amount of accuracy as those with the other salts, as the specimens used were not specially purified. Four samples were prepared by drying the hydrated salt at 200° till constant; No. 3093 appears to give results 81 cal. above those of the other samples, and this amount has consequently been subtracted in Table XII, which contains the results.

A few experiments were performed with the monhydrated sulphates of magnesium, copper, and lithium. Details of the preparation of the four different samples of the first of these will be found in the Trans., 1885, 100. The copper salt, of which one specimen was used, was prepared by heating the crystallised sulphate at 100°.

Two different specimens of the lithium sulphate were used in the different experiments with that salt.

Calorimetric Results. Explanation of the Tables (*p.* 291, *et seq.*).

All the determinations of the heat of dissolution are collected in the accompanying tables.

The thermometers employed are designated for brevity sake as 80, 81, 83, 84, 16, 39, and 616 respectively.

w is the weight *in vacuo* of the salt taken, W the water equivalent of the calorimeter and its contents, the actual water being $601{\cdot}687 + 0{\cdot}016T°$ C. c.c. (reckoned as so many grams with sp. heat = 1) together with that (if any) which the salt contained.

T is the temperature of the salt before its introduction into the calorimeter, expressed in degrees of the same thermometer as that employed in this latter.

t and t' are the corrected initial and final temperatures of the calorimetric liquid given in the arbitrary degrees of the thermometers employed, the corrections include* that due to the temperature of the salt introduced, the cooling (or heating) during its dissolution, the exposure of the column of mercury to the atmospheric temperature, and the calibration correction.

M represents the molecular heat of dissolution of the salt as given by the equation—

$$M = \frac{\left(\begin{matrix} t - t' \\ \text{or} \\ t' - t \end{matrix}\right) \alpha W M}{w},$$

* According to the equation $\dfrac{(t - T)wc}{W + w}$, c being the specific heat of the salt.

in which M is the molecular weight of the salt, and α the mean value of the thermometric degrees in degrees centigrade, these being for—

$$\begin{aligned} 80 &= 0{\cdot}39633 \\ 81 &= 0{\cdot}38663 \\ 83 &= 0{\cdot}38046 \\ 84 &= 0{\cdot}70659 \\ 16 &= 0{\cdot}38549 \\ 39 &= 0{\cdot}06025 \\ 616 &= 0{\cdot}064161 \end{aligned}$$

The corrections which are applied to M in certain cases will be understood from what has already been mentioned.

In the case of a hydrated salt, the observed heat of dissolution is represented by m, M being reserved for the "true" heat of dissolution $= m - xl_m$, l_m being the heat of fusion of 1 gram-mol. of ice.

The last column gives the initial temperature of the experiment in degrees centigrade, T. Where the mean results to which this temperature applies are deduced from experiments in which the various initial temperatures differed by more than about 0·08°, the centigrade equivalent of each is given in the column under t.

In most cases, the means are arithmetical means, but in a few instances some determinations have been allowed a smaller weight than others. With hydrated sodium sulphate, experiments with sample 3418 have been allowed twice the value of the others.*

Explanation of the Plates.

The calorimetric results are given diagrammatically in the accompanying plates; each of these plates contains three curves, one representing the apparent heat of dissolution of the hydrated salt, the second, to which the numbers on the right hand side refer, its "true" heat of dissolution, and the third, to which the numbers on the left refer, the heat of dissolution of the anhydrous salt. The continuous thick lines represent the mean results given in the tables, the others will be explained shortly. The higher the position of a point in any of these curves, the greater is the heat development or the less the heat absorption which it represents.

From the manner in which the curves are arranged, the vertical distance between any points in those representing the heat of dissolution of the salt in its hydrated and anhydrous conditions is proportional to the heat of combination of the salt with its water of

* Some of the numbers given in these tables will exhibit slight differences from those quoted in previous papers. The present ones are the more accurate, as they depend on a more correct calculation of the scales of the thermometers, and on a larger number of experiments.

crystallisation in the solid state. The values deduced for this latter are represented separately in the curves at the foot of each plate.

Critical Examination of the Results.

The most striking and most important feature of these curves is undoubtedly their irregularity. In all of them, there appear more or less sudden breaks, or else they consist of two or more independent curves.

Before discussing them, and the conclusions which may be drawn from them, it will be necessary to show the means which have been taken to make certain that these irregularities cannot be attributed to experimental error, an explanation which will but naturally suggest itself, when it is observed that an appropriate distribution of such an error of less than 100 cal. would cause most of these irregularities to disappear, and that even duplicate experiments at the same temperature will sometimes differ by nearly this amount.

The two thermometers 81 and 83 were alone employed in the first experiments, and the portion of the curves where the irregularities most generally occur, and where they were first noticed, coincides unfortunately with the point where one instrument was substituted for the other (at about 13—15°). The conclusion drawn at first was, of course, that the non-concordance of the instruments was the explanation of these irregularities. Many considerations, however, render such an explanation highly improbable.

(1.) The temperature at which the instruments were changed being notified by a bar across the curves, it will be seen that, although a sudden dip near this point is generally due to the experiments with the highest portion of 83, it is not always so; with $MgSO_4$ the dip is due to experiments with 81, while in the case of Na_2SO_4, $Na_2SO_4 10H_2O$, and $CuK_2(SO_4)_2$, there is no such dip noticeable, and with both $MgK_2(SO_4)_2$ and $MgK_2(SO_4)_2,6H_2O$ the point in question was investigated with both the instruments, and both of them gave identical results.

(2.) Were the irregularities in the curve belonging to the hydrated salt due to errors in the scale of the thermometers, irregularities of an exactly opposite nature would present themselves at nearly the same point in the curve of the anhydrous salt, but the reverse is the case. The depressions or elevations in the one are generally more or less reproduced in the other. If we were to apply corrections to the thermometers such as would reduce any one curve to uniformity, it would only bring into greater prominence the irregularities of the other curves. Besides which, the errors in the calibration curves which would have to be supposed to exist would be out of all proportion to the known magnitude of the probable error from this cause (see *Phil. Mag.*, 1886, **21**, 181).

(3.) The fact that these depressions do not always occur at the same temperature in the different cases, and that others at totally different temperatures exist, would alone be sufficient to disprove their being attributable to such a source.

However, that no proof should be wanting, another thermometer, No. 16, in which this debatable point occurred in the middle of the scale, was introduced, and fresh experiments performed with it. With potassium magnesium sulphate, both hydrated and anhydrous, a whole series were performed in which it was used simultaneously with one of the other instruments; the results with 16 only are (Plate III) represented by a thinner line, and bring out the peculiarities of the curve even more strongly than those with the other thermometers, which form the dotted curve, and in which the individual experiments are marked by crosses. The determinations at 15° were repeated thrice with 16, and the mean result here depends on as many as 8 observed values. For the sake of greater security, the experiments with the anhydrous and hydrated salt at the same temperature were performed within half an hour of each other.

With hydrated sodium sulphate (Plate V), 16 was also used, and the results with it are indicated as in the foregoing case. Except at 12·3°, where a considerable divergence unfortunately occurs, these results are concordant with those of the other instruments to the most minute details.

Experiments with this thermometer were also performed in the case of hydrated copper sulphate, hydrated magnesium sulphate, and potassium sulphate, and agreed fully with those with the other instruments, as will be seen from the tables, but their number was not sufficient to make it worth while representing them separately in the Plates.

In spite of these results, I did not yet feel satisfied, so remarkable did the facts appear to me; and, consequently, started fresh series of experiments with two instruments, 80 and 82, companion ones to 81 and 83, together with a third new one, 84, embracing all the temperatures required; what experiments were done with them were confined chiefly to potassium sulphate, and will be found to be thoroughly concordant with the others. But before the work with these had progressed very far, the idea occurred of using the same portion of the same instrument, and that a very much more delicate one, for every experiment. All doubt as to the irregularities being due to imperfections in the thermometers were thus set at rest effectually. This instrument, 39, which has been described above, was applied in the case of hydrated magnesium sulphate, anhydrous copper sulphate, potassium sulphate, and anhydrous sodium sulphate (Plates I, II, V, and VI); except with the latter salt, the results with

it only are represented separately by thin lines; the dotted curves representing those with the other instruments, and as will be seen they bear out in every case the conclusions which had been arrived at with the others, the results with 83 would appear to be generally rather high in comparison with those of 39, but the main features of the two are identical. The dotted curve given with copper sulphate refers to three experiments with No. 616.

Such, then, are the means I have taken for assuring myself of the correctness of these observations. But it is impossible by a mere description in outline, or by the synoptical view presented by experiments massed together in tables or diagrams, to convey any adequate conception of the strength of this assurance: of how the few experiments which first had exhibited any irregularity were repeated over and over again, after long intervals of time, with different instruments and with different samples; of how often the work, after being laid aside as complete, would slowly assume the appearance of a phantom conjured up by imperfections in the instruments, and of how often, having been begun all over again, such an idea would be dispelled, and conviction in the accuracy of the results enforced with double power. And now, it is only after having fully investigated all the imperfections of thermometers themselves, having obtained some more delicate and more perfect instruments than any yet produced, and having devised a method of using them which obviates the greater part of the experimental error, that I venture to bring the results before this Society.

Hydrates in Solution.

A cursory inspection of these curves will show that many of them must be still very imperfect. The changes in them are often confined within such narrow limits that, but for the chance selection of some particular temperature for an experiment, this change would never have been detected. The number of observations which would be necessary to establish satisfactorily the precise form of all the lines would be enormous; and it must, therefore, be remembered that, with the materials at present available, numerous as are the complications exhibited, they may in reality be far more so.

Considering, in the first place, what conclusions may be drawn from the examination of any one curve by itself, it will be seen that in no case is the heat of dissolution, whether of a hydrated or anhydrous salt, capable of being represented by a straight line, as is generally assumed (see Berthelot, *Ann. Chim. Phys.*, **29**, 310), nor even by a single curve (except perhaps in the case of Na_2SO_4 and $CuK_2(SO_4)_2$, though probably not so in either of these cases). With some of the an-

hydrous salts taken, this discontinuity might be attributed to variation in their heat of combination with those molecules of water with which they are associated in the solid form, but with hydrated salts no such explanation is possible, and we will take these, therefore, as presenting the more simple problem.

At certain points, then, in these curves there is a more or less sudden increase in the heat developed, and it seems impossible to account for such an increase in any way except by the formation of some new and higher hydrate.

What is generally termed the "hydrate" theory of solution may probably be incapable of giving a full explanation of all the phenomena of dissolution, but it is, I think, proved by overwhelming evidence that many salts in solution do exist in a state of combination with water, and it is highly probable that the hydrates which are there present are often of a higher order than those known in an isolated or solid form; that such is the case with the so-called hydracids and alkalis, Berthelot's researches on the heat developed when they are diluted with varying amounts of water have shown, and they have also shown that the same substance may form more than one such hydrate under different conditions, whilst under intermediate conditions these different hydrates coexist in a state of partial dissociation. The same state of things would appear to hold good in this case as regards salts, the agent which determines their formation being heat instead of excess of water. From a study of any of these curves, it would seem that as the temperature rises the amount of the particular hydrate present reaches a maximum at a certain point and then diminishes, thus producing a curve, when a further rise induces a different state of equilibrium, and another hydrate begins to form causing a fresh development of heat.*

This explanation, the only one which seems possible, involving the idea that an increase of temperature favours a higher combination between a salt and water, will at first sight appear to be opposed to our general ideas on the subject; but it must be remembered that we ought to have no general ideas on this subject at all, for we have no general knowledge on which to found them. We know, in the case of sodium sulphate and a few other salts, that a certain temperature,

* Instead of the amount of the hydrate, or the number of water molecules constituting it, being the variable quantity, it might be the energy with which the water in any *one* hydrate is combined with the salt. But this I consider to be improbable, for, as will be shown below, the temperatures at which an *increase* in the heat of dissolution of a salt occurs, are those at which a *decrease* in the energy of combination of the salt with its water of crystallisation takes place; moreover, any increase in this latter quantity is very small in comparison with the *general* increase in the heat of dissolution of a salt as the temperature rises, and could not afford any explanation of it.

generally a high one with reference to the salt in question, favours the dissociation of the salt from the water with which it is combined while in solution, or rather, that the balance of the many forces which the temperature influences results in the dissociation of the hydrate: but whether this be so in all cases, or whether it holds good also for the temperatures far below the melting point of the salt or the boiling point of the solution, we know not, and in the face of this absence of all evidence to the contrary, the present experiments must be accepted as proof. A striking point in favour of such a view is found in the case of sodium sulphate itself, where, instead of having any increased development of heat at about 14° and 23°, as in other cases, none occurs after 8°, that is, at a temperature 26° below that at which the affinity of the salt for water is known to diminish; the minor irregularities which occur in this curve at higher temperatures being probably due to experimental errors.

One case which was investigated with great care was that of potassium sulphate, owing to its being an anhydrous salt in every condition as far as is known, and one which, judging by the large absorption of heat on its dissolution, possesses but small affinity for water. As many as 58 experiments, many of them with two thermometers, were made; the delicate instrument 39 was used in 18 cases, and the results with it fully confirmed the previous ones, both as to the existence of a dip at 14°, where eight separate determinations were made, and as to the curvature of the line above and below this point (Plate VI). Only at 19° are the experiments not altogether concordant, and it may be that another dip occurs here, the curvature between this point downwards to 14° being more marked so as to pass through the experiment at 16·9°. However this may be, the existence of at least two curves and therefore two different hydrated conditions seems certain. (The results with thermometer 39, below about 13°, give results uniformly lower than those with the other thermometers, as has already been noticed.) Side by side with the potassium sulphate curve in Plate VI is given that of lithium sulphate, as well as a reproduction of that of anhydrous sodium sulphate. These three curves will be seen to exhibit no stronger resemblances to each other than they do to those of less closely allied salts. Lithium sulphate, like the potassium salt, shows a dip at about 14°, but in other respects the two cases are dissimilar, especially at the lower temperatures, while sodium sulphate differs from both of them, the portion at 14°, and indeed that from 12—17°, being somewhat higher, rather than lower, than the rest of the curve. It will have been seen that a considerable number of experiments were performed in the case of this salt, Table IX.

The experiment with lithium sulphate at 23° is not in accordance

with the rest of the curve; for this, a sample of the salt was employed which was not used in any other experiments, and it may have differed from the other samples in purity; none of the experiments, indeed, with this salt can be regarded as being of such an accurate nature as those with the other salts (see p. 271).

No conclusions can be drawn as to the universality of a dip in the curves at about 14°. It occurs in most of the present cases, it is true, but it must be remembered that we are dealing with salts all belonging to the same class, and that in the one which differs most from its congeners—sodium sulphate—such a dip as we have just said is absent; the precise point also at which it occurs is not identical in every case, and the peculiarities which the various curves exhibit at other temperatures are quite sufficient to differentiate them.

The salt which exhibits the greatest number of changes, and one in which these changes have been well established, is hydrated potassium magnesium sulphate (Plate III). The heat of dissolution of this salt between 2° and 24° constitutes no less than three complete curves, together with the beginning of a fourth one, the temperatures where minima heat developments are observed being 2° (perhaps lower in this case), 7·5°, 15°, and 24·3°. The increase which occurs after the latter temperature caused the case of magnesium sulphate to be investigated at these higher temperatures also, and an analogous rise was discovered, beginning, however, at a lower point, about 22°. But magnesium sulphate, unlike its double salt, exhibits no minimum point at 7·5°, the heat developed from 14° down to 3° forming but one continuous curve. It should be remarked that the same confidence cannot be placed in the experiments at very low temperatures as in the other cases, the great difficulty of keeping the temperature of the laboratory constant within a few degrees of zero, and the great effect which the presence of the operator has on the temperature of the calorimeter, rendering the operations less trustworthy.

The curves formed by the copper salts (Plates II and IV) differ very considerably from those of the magnesium salts; the changes which occur are much more abrupt in their nature; those of hydrated copper sulphate, and of the hydrated double sulphate would appear to consist of a series of straight lines rather than curves, and the true heat of dissolution of hydrated copper sulphate is affected by temperature to a considerably smaller extent than is magnesium sulphate, or indeed any of the other salts examined. It must be noticed, however, that, with the exception of anhydrous copper sulphate, these copper salts were not investigated so fully as the magnesium ones.

It is somewhat remarkable that in no case does any marked change appear at 4°, the temperature of the maximum density of water.

It is curious that the extent to which the *apparent* heat of dissolution of all three of the hydrated single sulphates varies with the temperature is very small, it being in some cases practically constant for a considerable range of temperature. This, however, is not so with the double sulphates; it would appear as if the potassium sulphate which is present in them still retained its individuality to a considerable extent, its heat of dissolution when combined in the double salt being affected in the same way, though not to the same extent, as when in the free state.

The true "molecular" nature of these double salts is also brought into prominence by the fact that in order to render the curves of their heats of dissolution analogous to those of the single salts, we must, as has been done in these tables, represent the heat evolved on half the scale only. We would almost appear to be dealing with two molecules instead of one, and thus getting a double rate of variation as the temperature falls or rises.*

It should also be remarked that what is here called the "true heat of dissolution" of both hydrated copper sulphate and hydrated magnesium sulphate is a positive quantity of no mean value, and that such a quantity even does not represent what is in reality the "true" heat of dissolution of the hydrated salt; for from it should be subtracted the heat of fusion of the salt itself, at present an unknown quantity. If the heat thus evolved be due to the combination of the already hydrated salt with more water—and it is difficult to find any other explanation of such an evolution—either this additional water must be considerable in amount, or else the energy with which it is combined must be great, and bear no small ratio to that with which the water of crystallisation is combined.

The series of curves referring to any particular salt are of too rough a character, and their precise meaning too imperfectly understood, to render it profitable to draw further conclusions from them; but with more complete data and more perfect knowledge, it would evidently be possible by prolonging them to obtain numeric values of the heat of formation of each fresh hydrate, and it would appear possible, if not probable, that this heat would not bear any very inconsiderable ratio to that of the formation of the known hydrates, it being thus unnecessary to imagine that the new ones are of a much more complicated character than those already known.

The occurrence of these successive changes in the constitution of a salt in solution, involving successive developments of heat, will involve also successive variations in the specific heat of the solution,

* This is in reality a consequence of the heat of formation of these salts being affected to only a small extent by temperature, and hence also of their specific heats being practically equal to the sum of those of the constituent sulphates (see p. 288).

too small no doubt to be rendered apparent by the imperfect means which we possess at present for its direct estimation, but none the less certain notwithstanding. We thus have a curious picture of the temperature of a saline solution rising under the influence of a constant source of heat, not with a regular motion, but in a series of pulsations, recurring at irregular intervals, often considerably less than 10° apart.

Water of Crystallisation.

We now pass to a consideration of those conclusions which may be drawn from a comparison of the curves of a salt in the hydrated and anhydrous condition. The difference between the quantities which they represent give the heat of combination of the salt with its water of crystallisation; this, it must be clearly understood, refers simply to the *known solid hydrate*, and is entirely independent of the combinations existing in solution.

The results are given in the lower diagrams in the various plates. An inspection of these will show that the heat of this combination is not a constant quantity, it does not even vary in any regular manner, but resembles in nature the heat of dissolution of a salt.

There appears in the first place to be a general tendency towards an increase in the energy with which the salt and water are combined, and such a tendency is in full accordance with the fact already observed of higher hydrates being formed in solution as the temperature is increased. It may be objected that here at any rate we know that a rise of temperature favours loss of water with a solid hydrated salt; but this knowledge, if it can be called such, is derived from experiments at considerably higher temperatures than any here dealt with, and, as far as I know, in none of these observations has the effect of temperature only, or the influence of temperature on the one factor, with elimination of its effects on other concomitant factors, been ascertained. When a salt is heated in air under ordinary conditions, it may be the increased avidity for moisture with which the air becomes endowed, and not any dissociating influence of the temperature itself, which causes the salt to part with its water. Or the loss may occur not because the energy with which it is combined is diminished, but because other tendencies, those towards different arrangements of the atoms in the molecule, for instance, are increased. In the present experiments such possibilities, however, are eliminated, since their results depend on the difference between two quantities which in every respect but one are precisely similar; in every case we have identical initial and final states; such experiments, therefore, are the only ones which can be admitted as evidence on the subject, and the evidence which they bear is not, I

think, much opposed to our general and unauthorised notions on the question, when we remember the lowness of the temperatures with which we are dealing, and when we notice that in the case of sodium sulphate, an increase in these temperatures, low as regards a thermometer, but high as regards the salt, causes a rapid *fall* instead of *rise* in the energy of the combination after about 15°.

In addition to all this, it must be pointed out that we are but observing in the case of these so-called molecular compounds a condition which has been well established in the case of many atomic compounds. A sufficiently high temperature will dissociate the constituents of water; but, nevertheless, the heat of their combination (the water being in the gaseous state) *increases* with the temperature, or does so at any rate at all those temperatures where we have any knowledge of the specific heats of the substances concerned. It is quite possible, and, indeed, unless some great changes in specific heats occur, must often be, that, even when a substance is actually partially dissociated, the heat of combination of its constituents in those compound molecules still existing, is *greater* than it is at lower temperatures when no dissociation exists; the heat and the energy of the combination of the constituents being, as a matter of fact, but one of the many factors which determine this dissociation.

It must be borne in mind that the variations in the heat of combination of the salt with its water cannot be looked upon as being so accurately determined as those of the heat of dissolution of the hydrated salt, for they depend on the values of two quantities instead of one. It would be rash to state that the break at 14° in the case of $MgSO_4,7H_2O$ for instance (Plate I), is not due to experimental error; it is but faintly marked in the mean curve, and by taking the different results of the different thermometers its appearance is very much altered; moreover, the number of determinations with the anhydrous salt were not large.

With copper sulphate (Plate II), however, it is otherwise. The heat of combination between 2° and 23° is represented by two complete curves and a portion of a third; the curves are steep, and throughout there is a tendency towards a rapid increase in the heat of combination. The first curve, that extending from 2° to 9° (and to a certain extent the second curve also), will be seen to be due chiefly to the peculiarities exhibited in the heat of dissolution of the anhydrous salt, and, in spite of the large number of determinations which were made between 4° and 9° with this salt, I cannot feel altogether satisfied as to it. The results with the delicate thermometer 39 (the thin line) reduce considerably the curvature at 6° which was given by the other instruments (the thick dotted line); but still it is well marked, and it should be remarked that an extra precaution was generally taken here of using

the salt contained in any one of the sealed tubes in which it was kept at two or three *different* temperatures, and performing the experiments consecutively. Three experiments performed with the most perfect thermometer (616, the thin dotted line) exhibited no curvature at all, but they are inexplicable by the side of the others, and the general inclination of the curve. Of the existence of a second curve from 9—17°, and a portion of a third one from 17—23°, there can, however, be no doubt. A marked similarity also appears between the various curves; allowing for experimental irregularities, the inclination of the rising and falling portions of each is the same, while a gradual increase in extent prevails throughout them.

Coming now to the double salts, it will be found that similar irregularities exist in the case of potassium magnesium sulphate (Plate III). The heat of combination is represented by one curve from 4—11°, by another less abrupt one from 11° to about 19°, from which point a third curve would seem to start; the results with thermometer 16 are given in the thin line side by side with those of the other instruments (the dotted line), and it will be seen that while they exaggerate some of the features, they make others less apparent, and show clearly the futility of insisting on every minute detail in the curves, and the necessity for considering their general bearings only.

With this salt, however, and also with sodium sulphate, more weight may be attached to the results at present under discussion than in the case of the other salts, for the curves of both the hydrated and anhydrous salts were investigated with the same degree of care. With the magnesium potassium sulphate the extra precaution was adopted in one series of experiments of effecting the determinations with the hydrated and anhydrous compound as nearly as possible at the same time.

With potassium copper sulphate (Plate IV) we have a line of a totally different nature to that of the corresponding magnesium salt; a short sharp curve exists between 13° and 15°, which would be looked upon with suspicion, were it not that this temperature evidently forms a starting point for a different order of conditions; the inclination of the line being totally different after it from what it is before. The straightness of the two portions of the line is remarkable, as also is the abruptness of the change; this abruptness appears throughout to be a characteristic of the copper salts in contradistinction to those of magnesium.

It should not be forgotten that the scale on which these curves of the double sulphates are represented is only half that used for the single salt, their peculiarities are therefore diminished. They will be found in Plate VII on the larger scale.

The only other case to mention is that of sodium sulphate (Plate V), and here we have a curve of a very different character from those of the other salts. There is a sharp increase in the heat of combination from 5° to 8° followed by as sharp a decline, another slight rise occurs afterwards as far as 13°; after this, the heat remains constant for the next two or three degrees, and then declines regularly to the end, instead of rising as it does in most of the other cases. Such I interpret the nature of this curve to be: if we take the results of thermometer 16 at 12°, where there is unfortunately some error with one of the instruments, and use it on all the details exhibited at higher temperatures, we should get the excrescence at 8°, repeated in a less marked manner at 12°, and again more feebly still at 16·5°, with a shadow of a third repetition at 21°; but although the results of the different instruments are remarkably concordant (except at 12°), the variations causing the irregularities at the higher temperatures are so slight that they may be attributed to experimental error, though, it is true, the number of experiments at each point is considerable; at any rate it is safer not to insist on their actual existence.

The curve of the anhydrous salt was examined with special care in the case of sodium sulphate in order to ascertain whether it exhibited any peculiarities at those temperatures where the hydrated salt did so, but no such resemblance even of the faintest description could be traced anywhere. Indeed, the only indication which exists of the anhydrous salt not giving a continuous curve throughout is that the portion between 12° and 17° is decidedly higher than the rest of the line.

The experiments with the monohydrated sulphates quoted in Table XIII are too few in number to give much weight to any conclusions drawn from them, but, such as they are, they tend to show that the same irregularities exist in the heat of formation of the lower hydrates as in that of the higher ones. The copper salt, however, is the only one where the temperature was varied sufficiently for such purposes.

The following are the values which may be deduced in the various cases:—

(1.) For $CuSO_4 + H_2O$ (solid)—

At 13·00°, 5615 cal.; at 17·83°, 5743 cal.; and at 22·88°, 5914 cal.,

numbers showing a rapid increase in the heat of combination with the temperature, as with the pentahydrated salt, though not at a regular, but at an increasing rate, this rate being 26·5 cal. per degree between the first and second temperature, and 33·8 between the second and third.

(2.) For $MgSO_4 + H_2O$ (solid)—

7012 cal. at 22·3°.

(3.) For $Li_2SO_4 + H_2O$ (solid)—

At 13·8°, 1267 cal.; and at 12·97°, 1417 cal. Mean, 1342 cal. at 13·39°;

to this latter, however, no very special value is to be attached (see p. 271).

Here, then, we have a series of changes analogous to those taking place in saline solutions, but more remarkable, inasmuch as the substances which exhibit them undergo no change in centesimal composition.

That changes of temperature bring about changes in the constitution, not only of complex molecules such as those of hydrated salts, but of the more simple bodies which are termed atomic compounds, as well as of the elements themselves, is already well known in some few cases; but the universality of these changes, and the frequency of their occurrence, is a totally new feature.

Our ideas of the stability of a compound must be considerably modified; we must recognise that the substance which we are dealing with at one temperature may be totally different in constitution from the same substance at a temperature only 10° higher or lower. These changes can only be attributed to alterations in the relations between the various atoms or molecules in the hydrated salt. They cannot be explained by changes in the grouping of the many molecules which (probably) act as physical units, for the nature of the determinations eliminates entirely the influence of any such changes. These variations in the heat of combination of the components of the molecule will, as in the case of solutions, necessitate slight corresponding changes in the specific heat of the substance, and we shall consequently have the temperature of the salt under a constant source of heat, rising in an undulatory instead of a regular manner.

One other very important feature remains to be noticed. On referring to the plates, it will be seen that the high portions in those curves which represent the heat of combination of the salt with its water of crystallisation, coincide with the low portions in those representing the heat developed in the dissolution of that salt, and *vice versâ*; the stronger the energy with which the few molecules of water in the solid salt are retained, the smaller is the number of molecules in the liquid hydrate. It would appear as if a rise of temperature causes an increase in the energy of the combination of the water with the salt up to certain point, but that a further increase, instead of raising this energy still higher, takes a different direction, and endows the salt with a capacity for taking up a larger number of molecules; but inasmuch as the amount of water held is now greater, each individual portion of it is held with diminished

energy. Such would appear to be the case, but it is not possible to affirm it with confidence, for we are not studying the salt in the same state in both cases; in one case it is in the solid, and in the other in the liquid condition; but another instance of a like nature, not open to such objections, will be brought forward shortly, and the strong presumptive evidence which we have here for supposing the relations between certain portions of a molecule to be influenced by a further addition to it, is one which is certainly in accordance with our general ideas on "atomic" compounds, and one which I have elsewhere (*J. Chem. Soc.*, Abstr. of Proceedings, 1885-6, 112) argued on other grounds to hold good with reference to water of hydration.

It will follow from the fact that the heat of combination of a salt with its water is not a constant quantity, that the specific heat of the hydrated salt is not exactly equal to the sum of those of the anhydrous salt and water (solid) in it. This conclusion will hold good even if we assume an error to have occurred in the number taken for the specific heat of ice at these high temperatures (see p. 262), for, not to mention the irregularities in the curves themselves, the application of a correction in this latter, such as would reduce the curve (*i.e.*, that of the heat of combination) to a horizontal line in one case, would only increase its divergence from such a line in another (*cf.* the latter portions of the copper sulphate and sodium sulphate curves).

The general tendency exhibited in the majority of cases being in the direction of an increase of the heat of combination with a rise of temperature, it follows (p. 260) that the specific heat of the hydrated salt will be somewhat *less* than the sum of those of the solid water and anhydrous salt. It is difficult, however, to speak with any certainty of these "general tendencies," for the range of temperatures in the present experiments is very small in comparison with that through which the salt is capable of existing.

An inspection of the numbers given for the specific heats of salts, and the great differences in those obtained by different observers, will make it apparent why any direct determinations of these specific heats should have failed in elucidating these facts.

It will be necessary to stop for a moment to enquire what effect a more accurate method of calculation, and a more perfect knowledge of the data on which those calculations were based, might have on the general conclusions arrived at here.

To begin with, it is only by assuming sudden alterations in the specific heat of an anhydrous salt, or of ice, that the alterations in the curves here given could be eliminated. Such alterations would involve similar conclusions as regards the constitution of the salt (or of ice), as we have here drawn as to that of the hydrated salt, and would thus be but a poor explanation. The fact that the curves of

the true heat of dissolution of the hydrated salt preserve a course so nearly parallel to those of the anhydrous salts in most cases, and that they converge to a considerable extent in the case of sodium sulphate (the only case in which we have extraneous reasons for expecting that they would converge, *i.e.*, that a rise in the temperature would diminish the energy with which the solid salt retains its water), is strong evidence that the water in a crystallised salt is *solid* water, and that in the dissolved salt is liquid water, and also that the numbers which we have taken for the heat of fusion of this solid water are very near the truth.

Secondly, what would be the general drift of the error caused by taking the volume of the solution as being equivalent to so many grams with a sp. heat of unity instead of basing the calculations on the actual sp. heat of the solution. On p. 267, where copper sulphate was taken as an instance, the error being greater in its case than in any other, it was shown that, as far as we could judge from the very imperfect data at our disposal, whatever the error in the actual quantities might be, the relative error in the comparison of two experiments at 4° and 24° respectively, would be but $\frac{1}{1500}$th; the sp. heat of the solution at the latter temperature by comparison with the sp. heat at the former would be under-estimated by that amount. Referring to Plate II, we see that 16700 cal. is the heat of dissolution of the anhydrous salt as given at 24°, it therefore ought to have been $\frac{1}{1500}$th greater, *i.e.*, 16810 cal.; in the same way, the apparent heat of dissolution of the hydrated salt should have been -2820 instead of -2800, giving for its "true" heat of dissolution 5340 instead of 5360; the correction of the calculations would thus give $(16810 - 5340 =)$ 11470 cal., as the heat of combination of the solid with its water, instead of $(16700 - 5360 =)$ 11340 cal. which was the value taken. A more correct method of calculation would thus only bring out into stronger prominence the increase in this latter quantity as the temperature rises.

Lastly, these experiments themselves have shown the existence of a more subtle source of error, and one which it is impossible to allow for. The initial temperature of the water is that at which the dissolution must be regarded as being effected, the final temperature serving only as a means of measuring the heat developed; but the proper use of this final temperature depends on our knowledge of the sp. heat of the solution between it and the initial temperature, and, owing to the variations here exhibited in this, it will not be the same for the interval from t to t' when t' is higher than t, as it is for a like interval when t' is below t, *i.e.*, when dissolving the anhydrous and hydrated salts at the same initial temperatures we shall generally be using liquids possessing different sp. heats in the

two cases. Taking as an instance experiments at 16° with potassium magnesium sulphate, and remembering that it is the curve of the hydrated salt which gives a representation of the sp. heat of the solution, this point 16° occurs where the curve is rising, *i.e.*, where an increased development of heat and, therefore, a diminished sp. heat, is brought about by an increase in temperature. In the experiment here with the anhydrous salt, the *rise* measured from 16° to (say) 17° will have corresponded to a *smaller* development than the *fall*, measured in the case of the hydrated salt, from 16° to 15°, the former quantity will have been over-estimated, and the latter under-estimated, the individual experiment should have been plotted at the points marked A and B respectively; these in each case will be *lower* in the diagram, and, if the fall measured is of the same extent as the rise measured, they will be lower to the same extent, thus making no difference in the distance between them, *i.e.*, in the heat of the combination of the salt with its water as deduced from them. In other cases, where the rise and fall measured were not equal, an error will have occurred from this cause which may have resulted in the exaggeration or diminution of the peculiarities of this curve, but it will probably have been of very small extent, and will have affected the general nature of the curve but slightly.

Heat of Formation of Double Salts.

The experiments which have already been described afforded the means for the determination of another quantity, namely, the heat of combination of two sulphates to form the double sulphates, $MgK_2(SO_4)_2$ and $CuK_2(SO_4)_2$, in the solid state. Where x represents this amount, and M the molecular heat of dissolution of the two single and double sulphates—

$$x = (M_K + M_{Mg}) - M_{MgK} - N,$$

in which N represents the heat developed on mixing solutions of the constituent sulphates. This latter quantity has been measured by various physicists, and has been given by them as *nil* in the case of both copper sulphate and magnesium sulphate. A few fresh determinations of it are given in Table XIV. In order to render these determinations more accurate, blank experiments were interspersed with the others, and a small correction, which would appear to be generally necessary, owing to loss or gain of heat while the solutions were being mixed, was thus made.

The results bear out fully the conclusions of former experimenters as to the value of N being negligible, and consequently the heat of combination of the two sulphates in the double salt will be the difference between the heat of dissolution of the anhydrous double salt, and the

sum of those of its constituents in the anhydrous state also. The various values thus deduced for these quantities at different temperatures are plotted out into curves in Plate VII.

The general features shown in the case of the magnesium salt is that of two curves meeting at about 14° where the heat of combination is at a minimum; the portion between 2° and 6° would appear to form part of another curve; but in this case, more than in previous ones, we must not insist too stringently on the details which the lines exhibit, as each point in them is dependent on the correct estimation of three separate quantities, each of which is of considerable magnitude.

With the copper salt, we find a minimum reached at about the same temperature, 14°, the heat of combination decreasing gradually, and perhaps regularly, up to this point, after which it again increases, but at a very much greater rate.*

Here then, with the components of a double salt, we have the same remarkable variations in the energy of combination as we have between a salt and its water of crystallisation, and similar conclusions may be drawn from them.

Side by side with these curves are given those which represent the heat of combination of the same double salt with its water of hydration (drawn to the same scale as the former), and a comparison of the two leads to important conclusions. It will be seen that, with no exceptions other than what may be attributed to experimental error, the temperatures at which the one quantity attains a maximum is the temperature at which the other attains a minimum. This is very strikingly displayed in the cases of both salts, and fully bears out the conclusion which was drawn above, that the relationship between any two parts of a complex molecule is influenced by any change in the other parts of it. Here we appear to have a principle of compensation carried out between the various parts of the solid molecule, just as in the former case an increase of affinity exhibited by a salt in taking up a further supply of water, seemed to leave it but a smaller amount to be expended on that already attached to it.

Although this principle of intramolecular compensation may be more confidently affirmed from these experiments with the double salts than it was with the hydrated salts, it can yet be regarded only as strongly probable, and not absolutely proved: even here we are not dealing with the same molecule in both cases, for the heat of hydration

* Owing to a clerical error in a previous communication (this vol., 7 and 15), the heat of dissolution of copper sulphate was quoted as being 600 cal. less than it should have been, and the heat of formation of the double salt was consequently under-estimated to the same extent. The present numbers contain also some further corrections of an unimportant nature (see foot note, p. 272).

is measured in the hydrated salt, whereas the heat of combination of the other constituents is measured in the anhydrous salt. It is difficult to conceive, however, any means whereby a nearer approach to positive evidence could be obtained.

It will be noticed that with both pairs of curves in Plate VII, the one individual curve is determined from two quantities, and the other from three quantities, and that of these quantities one only (the heat of dissolution of the anhydrous salt) is common to the two; thus the data on which these two curves are based are to a considerable extent independent of each other.

Summary and Conclusion.

The main points of the present communication may be summarised as follows:—

1. The heat of dissolution of a salt at different temperatures is not represented by a straight line, but by a curve, or generally by a series of curves.

2. Each of these curves probably indicates the formation and existence of some fresh hydrate in the solution.

3. The formation of higher hydrates as the temperature rises would not appear to hold good when we approach a temperature which is near the melting point of the solid hydrated salt, as in the case of sodium sulphate.

4. From the constant variations in the thermal phenomena attending dissolution at different temperatures, it follows that the specific heats of saline solutions exhibit similar variations, remaining constant, or even varying at a uniform rate, throughout very limited ranges only.

5. The heat of combination of a salt with its water of crystallisation in the solid state undergoes similar series of changes.

6. From this it follows that the specific heat of such a salt is not a constant quantity, and that it is not exactly equal to the sum of that of the anhydrous salt and the solid water present, but is generally somewhat less.

7. The general tendency between 2° and 23° is towards an increase in the energy with which the water is combined.

8. Any temperature at which a higher hydrate is formed by a salt in solution, is marked by a *decrease* in the heat of combination of the salt with its water of crystallisation in the solid state.

9. The heat of combination of two sulphates to form a double salt is subject to variations of the same nature as that of the combination of a salt with water.

10. The variations in the heat of combination of the two salts is

attended by variations of an opposite sign in the heat of combination of the double salt and the water combined with it.

11. Most of the salts here investigated show some points of similarity in the curves which they yield, but each possesses specific peculiarities.

12. The peculiarities exhibited by a single salt appear to be reproduced to a certain extent in the double salts which they form, illustrated by the rise in the curves of both the magnesium salts at about 22°, and the character of abruptness displayed in the case of both the copper salts.

In drawing these conclusions care must be taken that they be not understood in too general a sense. The temperature of 14° appears, for instance, to correspond so often to a depression in the curves, that we might be led to attribute this depression to changes undergone by the water molecules themselves at this temperature; but it must be remembered that the salts which have been investigated belong not only to the same type, the sulphates, but chiefly also to the same class of that type, and that the one which differs most from the others in its nature (sodium sulphate) exhibits a totally different behaviour at this temperature; and even those salts which are most similar in their nature exhibit very marked differences at many temperatures in the heat of their dissolution.

It would indeed have been more satisfactory to have examined a greater variety of salts, and this would have been done had not the work been begun with a different object in view, and had it not progressed a considerable way towards its conclusion before its more important bearings became apparent. It is my hope, however, to extend the work at some future time, though the laborious and trying nature of it may prevent my doing so for some time; no form of apparatus has at present been devised whereby such experiments as these would not suffer in accuracy by being performed at temperatures other than that of the surrounding air, and the absolute dependence of one's work on the atmospheric conditions of a changeable climate, the great waste of time which its changes entail, together with the hardship of working for days together at temperatures but a few degrees above zero, and on other occasions in an atmosphere superheated some 20° or 25° by burning gas, and the constant attention requisite in maintaining these temperatures for a long period of time, render the work of a most laborious and unenviable description.

TABLE I.—*Heat of Dissolution of Anhydrous Magnesium Sulphate.* $MgSO_4 = 119{\cdot}76$; $\frac{3}{40}$ *mol.* $= 8{\cdot}982$ *grams.*

Sample.	w.	W.	Therm.	τ.	t.	t'.	$t' - t$.	M.				T.
1. 2718	9·098	614·27	81	33·18	32·201	38·836	6·635	20743				
2. 2754	9·007	614·27	81	35·40	32·306	38·890	6·584	20792			20724	22°·32C.
3. 2718 and 2754	8·974	614·27	81	35·80	32·416	38·927	6·511	(20637)				
4. 2754	8·417	614·20	81	19·71	19·835	25·880	6·045				20425	17·52
5. 2718	10·783	614·15	81	12·92 (14·685)	12·497	20·128	7·631	20139			20158	14·773
6. 3092	8·974	614·16	81	12·34 (14·85)	12·9215	19·288	6·3665	20178				
7. 2718	9·099	613·91	81	13·08 (13·44)	9·268	15·6635	6·3955	19980	19996			
8. 2718	9·105	613·91	81	13·24	9·301	15·712	6·411	20013				
9. 2754	9·128	613·91	81	12·70 (13·44)	9·267	15·711	6·444	20068	20028			
10. 2754	9·021	613·91	81	12·81	9·196	15·539	6·343	19988			20020	13·43
11. 2718	10·885	614·13	81	8·88 (13·37)	8·8935	16·563	7·4695		20051			
12. 2754	9·043	614·07	83	25·79	25·024	31·443	6·419				19860	10·53
13. 2754	8·813	614·00	83	13·10 (5·96)	13·0315	19·152	6·1205	19429			19420	5·98
14. 2718	9·105	614·15	83	14·37 (6·00)	13·076	19·391	6·315	19410				
15. 2718	10·157	613·94	83	7·68	3·208	10·086	6·878				18943	2·23
16. 2754	8·947	613·97	83	3·07	2·0835	8·106	6·0225				18830	1·80

TABLE II.—*Heat of Dissolution of Heptahydrated Magnesium Sulphate.* $MgSO_4,7H_2O = 245{\cdot}48$; $\frac{3}{40}$ *mol.* $= 18{\cdot}411$ *grams.*

Sample.	*w.*	W.	Therm.	*r.*	*t.*		*t'.*	*t − t'.*	*m.*			$7l_m$.	M.	T.
1. 3610	18·539	617·92	39	41·02	39·954		32·1345	7·8205	−3843		−3838	−11460	7622	24°·63 C.
2. 3610	18·509	617·90	39	40·38	41·641		33·8695	7·7715	−3834					
3. 2756	18·238	617·47	81	33·28	32·2605		31·0545	1·206	−3875					
4. 2756	18·470	617·59	81	33·47	32·2625	(22·32)	31·0145	1·248	−3960	−3915				
5. 2756	18·408	617·56	81	34·28	32·411		31·183	1·228	−3910		−3904	−11315	7411	22·278
6. 3610	18·554	617·89	39	40·22	40·457	(22·215)	32·587	7·870	−3865	−3887				
7. 3610	18·519	617·87	39	41·18	40·448		31·5015	7·9465	−3909					
8. 3610	18·498	617·83	39	40·63	40·333		32·408	7·825	−3853		−3861	−11180	7319	19·99
9. 3610	18·563	617·86	39	41·33	40·386		32·592	7·884	−3869					
10. 2756	18·629	619·61	81	22·21	19·8805	(17·575)	18·6725	1·208	−3822	−3868				
			16	—	30·127		28·883	1·241	−3915					
11. 3610	18·530	617·79	39	41·34	40·850	(17·55)	33·626	7·828	−3848	−3848	−3863	−11028	7165	17·543
12. 3610	18·527	617·79	39	39·74	40·563		33·3415	7·8255	−3847					
13. 3608	18·410	617·73	39	40·00	40·677	(17·52)	33·815	7·859	−3880	−3895				
14. 3608	18·558	617·82	39	40·13	40·4965		33·513	7·9805	−3910					
15. 3608	18·421	617·74	39	41·77	40·5945	(16·54)	32·6585	7·936	−3915	−3891				
16. 3608	18 511	617·79	39	41·57	40·0065		33·1325	7·874	−3867		−3885	−10968	7083	16·507
17. 3416	18·272	619 09	81	16·80	16·973	(16·44)	15·7615	1·2115	−3896	−3873				
			16	—	27·174		25·969	1·201	−3850					
18. 2756	18·464	617·44	81	12·54	12·9695		11·714	1·2555	−3984					
19. 2756	18·436	617·44	81	12·60	13·140	(14·93)	11·896	1·244	−3954	−3949				
20. 2756	18·447	617·44	81	12·91	13·1805		11·950	1·2305	−3909					
21. 2756	17·478	616·38	81	12·65	13·1635	(14·95)	11·9705	1·193	−3993	−4009	−3956	−10871	6915	14·828
			16	—	23·3595		22·1535	1·206	−4025					
22. 3608	18·456	617·72	39	42·86	41·086	(14·40)	33·1175	7·9785		−3924				

TABLE II.—(*continued.*)

Sample.	w.	W.	Therm.	τ.	t.		t'.	$t-t'$.	m.			$7l_m$.	M.	T.
23. 2756	17·503	618·66	83	32·92	33·041	(13·57)	31·838	1·208	−3971	−3962				
			16	—	19·837		18·655	1·182	−3954					
24. 2756	18·072	618·92	83	27·97	31·657	(13·05)	30·399	1·258	−4024	−4018				
			16	—	18·480		17·242	1·238	−4012		−4013	−10772	6759	13°·139 C.
25. 3608	18·424	617·64	39	41·47	40·546	(13·13)	32·3665	8·1795	−4014	−4020				
26. 3608	18·533	617·69	39	40·43	40·646		32·3995	8·2465	−4025					
27. 3608	18·416	617·60	39	42·66	40·872	(12·815)	32·6775	8·1945	−4044					
28. 3608	18·514	617·69	39	40·60	40·3885	(11·39)	32·1835	8·205	−4029	−4030				
29. 3608	18·404	617·64	39	41·00	40·586		32·423	8·163	−4030		−4006	−10655	6649	11·187
30. 2756	18·281	617·30	83	25·81	25·5125	(10·78)	24·2595	1·253	−3952					
31. 2688	19·726	634·34	83	19·52	16·840	(7·32)	15·4825	1·3575	−4077	−4076				
32. 2688	18·295	617·12	83	19·82	16·615		15·325	1·290	−4064					
33. 3416	15·520	617·55	83	17·12	16·968	(7·35)	15·877	1·091		−4054	−4036	−10425	6389	7·41
34. 2678	18·797	617·38	83	19·82	16·929	(7·4)	15·641	1·288	−3951	−3979				
35. 2678	18·896	617·62	83	19·92	17·742	(7·7)	16·4295	1·3125	−4007					
36. 2756	18·347	617·26	83	14·03	13·097		11·7895	1·3075			−4108	−10342	6234	6·00
37. 2756	16·217	616·11	83	2·84	5·3095	(3·04)	4·1165	1·193	−4233		−4202	−10154	5952	2·98
38. 2756	18·469	617·27	83	7·44	5·119	(2·93)	3·785	1·336	−4170					

TABLE III.—*Heat of Dissolution of Anhydrous Copper Sulphate.* $CuSO_4 = 158·84$; $\frac{3}{40}$ *mol.* = 11·913 *grams.*

Sample.	w.	W.	Therm.	r.	t.		t′.	t′ − t.	M.			T.
1. 2729	11·810	614·27	81	34·40	33·753		38·932	5·179	16543 + 160			
2. 2729	12·018	614·27	81	34·42	33·835		39·044	4·999	16351 + 160	16618		
3. 2729	12·008	614·29	81	34·84	33·863		39·107	5·244	16475 + 160		16630	22·92°C.
4. 3094	11·923	614·29	81	34·50	33·9445		39·208	5·2635		16654		
5. 2729	11·940	614·82	81	22·55	21·6205	(18·22)	26·7595	5·139	16235			
6. 3094	11·861	614·82	81	22·65	21·6215		26·7515	5·130	16314	16274	16222	17·96
7. 2729	11·958	614·11	81	16·10	19·582	(17·43)	24·6925	5·1105		16118		
8. 3094	11·840	614·17	81	21·84	16·8035		21·850	5·0465	16076		16082	16·36
9. 2729	11·873	614·17	81	18·36	16·8565		21·921	5·0645	16089			
10. 3401	12·063	614·16	81	13·29	13·662		18·771	5·109	15974		15994	15·135
11. 3401	12·095	614·18	81	13·58	13·623		18·758	5·135	16013			
12. 2729	11·747	614·10	83	32·70	33·016	(13·595)	38·002	4·986	15752 + 160	= 15912		
13. 3094	11·599	614·10	83	33·98	33·1615		38·146	4·9845		15955		
14. 3401	11·791	614·10	83	33·12	33·2465	(13·595)	38·311	5·0645	15940			
15. 3401	11·951	614·10	83	33·02	33·011		38·152	5·141	15964	15952	15929	13·57
16. 3401	11·921	615·93	83	38·05	33·014	(13·545)	38·104	5·090	15866	15826		
			81	—	9·619		14·607	4·988	15791			
17. 3609	11·990	614·39	39	13·97	11·853	(13·33)	44·2855	32·4325		15941		
18. 2729	11·900	614·01	83	34·08	30·4725	(12·60)	35·562	5·0895		15870	15836	12·56
19. 2729	11·928	614·10	83	28·95	30·2765	(12·52)	35·3045	5·028	15643 + 160	= 15803		
20. 3413	10·987	614·08	83	28·19	26·3975		31·4765	5·079	15724			
21. 3413	11·931	614·08	83	27·58	26·789		31·836	5·047	15697			
22. 3413	11·952	614·08	83	26·65	26·661	(11·12)	31·685	5·024	15599	15698		
23. 3413	11·994	614·08	83	26·76	26·5375		31·638	5·1005	15771			
24. 3414	11·945	614·05	83	25·52	25·4415		30·491	5·0495	15687			
25. 3414	11·988	614·05	83	25·71	25·4725	(10·70)	30·5365	5·064	15676	15670	15673	10·88
26. 3414	11·907	614·05	83	26·10	25·5085		30·5315	5·023	15655			
27. 3414	11·946	614·05	83	26·02	25·4225		30·4585	5·036	15644			
28. 3609	12·009	614·34	39	13·41	11·450	(10·77)	43·139	31·689	15622	15635		
29. 3609	11·844	614·34	39	13·21	11·910		43·156	31·246	15648			

TABLE III—(*continued.*)

Sample.	w.	W.	Therm.	r.	t.		t'.	$t' - t$.	M.				T.
30. 3612	12·042	608·44	616	13·67	14·648	(9·01)	46·621	29·973		15435			
31. 3611	12·059	608·18	39	9·49	12·085		44·074	31·989		15440			
32. 3609	11·876	614·32	39	12·92	11·812	(8·945)	42·9745	31·1625	15427	15429	15458		
33. 3609	11·859	614·32	39	16·06	12·182		43·299	31·117	15430				
34. 3609	11·979	614·32	39	13·11	11·776	(8·95)	43·340	31·564	15491	15502		15450	8°·951C.
35. 3609	12·265	614·39	39	8·02	11·690	(8·91)	44·5165	32·8265	15513				
36. 2729	11·865	614·05	83	20·37	20·819	(8·943)	25·7475	4·9285	15414	15427			
37. 2729	11·773	614·05	83	20·56	20·8595		25·7585	4·8980	15441		15439		
38. 2739	12·059	614·05	83	20·78	20·880	(8·927)	25·8605	4·9805	15291 + 160 =	15451			
39. 3094	11·987	614·05	83	21·37	20·7105		25·7015	4·991		15450			
40. 2729	11·875	614·00	83	14·26	14·170	(6·40)	19·0355	4·8645	15200 + 160 =	15360	15343		
41. 3427	12·025	614·00	83	13·22	14·107	(6·36)	19·0735	4·9665		15325			
42. 3612	12·047	608·40	616	13·28	13·9005	(6·125)	43·412	29·6115		15239			
43. 3611	11·493	608·14	39	11·89	12·6085	(6·07)	42·9245	30·316	15352				
44. 3611	11·968	608·14	39	12·76	12·395	(6·056)	43·736	31·341	15241	15284	15274	15300	6·099
45. 3611	11·970	614·28	39	6·28	11·518	(6·017)	42·586	31·068	15258				
46. 3609	11·874	614·28	39	14·63	12·119	(6·06)	42·980	30·861	15279	15276			
47. 3609	12·047	614·28	39	12·71	12·5405		43·734	31·2935	15273				
48. 2729	11·910	614·00	83	15·42	12·826	(5·93)	17·666	4·840	15169 + 160 =	15329	15337		
49. 3094	11·958	614·00	83	15·81	12·769		17·683	4·914		15345			
50. 3401	10·360	614·35	83	9·99	10·077	(4·83)	14·284	4·207		15076			
51. 3612	11·984	608·37	616	13·49	14·076	(4·13)	43·212	29·146	15079				
52. 3609	11·535	608·11	39	12·26	12·421	(4·05)	42·1425	29·7215	14995	15066			
53. 3611	11·945	608·11	39	10·02	12·143	(4·03)	42·979	30·836	15024			15001	4·08
54. 3401	10·900	614·33	83	8·74	7·591	(3·91)	12·0015	4·4105		15022			
55. 3413	12·073	613·96	83	5·34	6·6375	(3·54)	11·456	8·8185		14808			
56. 2729	11·838	613·95	83	1·63	3·183	(2·215)	7·8545	4·6715	14647 + 160 =	14807		14785	2·092
57. 3401	11·808	613·95	83	1·68	2·512	(1·97)	7·210	4·698		14762			

TABLE IV.—*Heat of Dissolution of Pentahydrated Copper Sulphate.* $CuSO_4,5H_2O = 248{\cdot}64$; $\frac{3}{40}$ *mol.* = 18·648 *grams.*

Sample.	w.	W.	Therm.	τ.	t.		t'.	$t - t'$.	m.			$5l_m$.	M.	T.
1. 2736	17·508	614·43	81	33·54	33·6585		32·830	0·8285	−2795		−2798	−8110	6312	22°·9 C.
2. 2736	18·241	614·69	81	34·61	33·792		32·927	0·865	−2802					
3. 2736	18·105	616·63	81	30·56	30·821		29·997	0·826	−2760		−2781	−8060	5279	21·75
			16	—	41·079		40·238	0·841	−2802					
4. 2736	18·326	614·59	81	18·81	22·551		21·691	0·860	−2772		−2762	−7921	5159	18·51
5. 2736	18·500	614·66	81	19·61	21·611	(18·56)	21·611	0·877	−2801					
6. 2736	18·742	614·82	81	22·28	21·840	(18·41)	20·9785	0·8615	−2717					
7. 2736	18·574	616·72	81	22·43	19·683		18·831	0·852	−2720		−2747	−7878	5131	17·47
			16	—	29·929		29·0575	0·8715	−2774					
8. 2736	18·756	616·51	81	16·90	16·984		16·0985	0·8855	−2798		−2796	−7833	5037	16·44
			16	—	27·196		26·309	0·887	−2794					
9. 2736	18·826	616·52	81	13·29	13·5935		12·6805	0·9135	−2876		−2857	−7777	4920	15·12
			16	—	23·782		22·878	0·904	−2838					
10. 2736	18·637	614·60	83	35·77	33·3965		32·466	0·9305	−2903	−2902	−2912	−7718	4806	13·71
11. 2736	18·555	614·57	83	35·77	33·354	(13·705)	32·428	0·926	−2901					
12. 2736	18·729	616·51	83	32·95	33·426	(13·725)	32·4745	0·9515	−2963	−2923				
			16	—	20·2045		19·291	0·9135	−2882					
13. 2736	18·464	616·30	83	28·24	29·128		28·2195	0·9085	−2869		−2888	−7645	4757	12·07
			16	—	15·972		15·063	0·909	−2908					
14. 2736	18·194	614·46	83	22·97	21·1225		20·1965	0·926	−2958		−2971	−7516	4545	9·00
15. 2736	19·165	614·80	83	20·27	20·7995		19·8165	0·983	−2983					
16. 2736	18·471	614·51	83	12·19	12·8875		11·924	0·9635	−3032		−3038	−7385	4347	5·95
17. 2736	18·854	614·61	83	20·75	13·052		12·0645	0·9875	−3045					
18. 2736	18·197	614·37	83	1·75	4·333		3·355	0·978			−3124	−7237	4113	2·66
19. 2736	17·867	614·18	83	2·67	3·837		2·844	0·993			−322[illegible]	−7227	4000	2·49

TABLE V.—*Heat of Dissolution of Anhydrous Potassium Magnesium Sulphate.* $MgSO_4,K_2SO_4 = 293{\cdot}64$; $\frac{3}{80}$ *mol.* = 11·012 *grams.*

Sample.	w.	W.	Therm.	τ.	t.	t′.	t′ − t.	M.	Correction.	M corrected.				T.
1. 3432	11·240	614·30	81	36·73	37·1605	39·008	1·8475	11475	+ 1113				12588	24°·22 C.
2. 3054	11·067	614·27	81	28·70	32·117	33·9495	1·8325	11559	+ 417	11976	12020			
3. 3054	11·094	614·27	81	28·88	32·1875	34·0385	1·851	11648	+ 417	12065				
4. 2796	11·184	614·27	81	36·36	32·324	34·234	1·910	11925	+ 120	12045				
5. 3000	11·049	614·27	81	35·00	32·0625	33·9515	1·889	11935	+ 54	11989	12055		12039	22·28
6. 2796 and 3000	11·011	614·27	81	32·77	32·230	34·134	1·904	12071	+ 87	12159				
7. 3039	11·140	614·27	81	31·53	32·2315	34·163	1·9315	—	—	12104	12027			
8. 3039	11·027	614·27	81	32·19	32·2285	34·116	1·8875	—	—	11949				
9. 3432	11·139	615·97	81	28·84	28·859	30·590	1·731	10878	+ 1113				11991	21·01
10. 3432	11·045	615·95	81	24·79	24·881	26·557	1·676	10621	+ 1113	11734			11719	19·48
			16	—	35·140	36·801	1·661	10592	+ 1113	11705				
11. 2796 and 3000	11·039	614·23	81	23·33	23·044	24·8685	1·8245	11537	+ 87				11624	18·775
12. 3432	11·168	615·92	81	20·37	19·676	21·330	1·654	10367	+ 1113	11480			11471	17·47
			16	—	29·916	31·572	1·656	10349	+ 1113	11462				
13. 3432	11·077	614·18	81	15·65	16·499	18·1115	1·6125	10161	+ 1113				11274	16·24
14. 2796 and 3000	11·058	614·14	81	13·01	13·178 (14·96)	14·9085	1·7305	10922	+ 87			11019		
15. 3432	11·021	615·88	81	12·54	13·065 (14·91)	14·6045	1·5395	9777	+ 1113	10890	10928		10963	14·94
			16	—	23·268	24·824	1·556	9853	+ 1113	10966		10950		
16. 3432	11·009	615·86	83	35·96	36·578 (14·93)	38·173	1·595	9978	+ 1113	11091	10973			
			16	—	23·353	24·890	1·537	9743	+ 1113	10855				
17. 3432	11·104	615·83	83	32·38	31·642	33·207	1·565	9706	+ 1113	10819			10764	13·06
			16	—	18·4625	19·9895	1·527	9596	+ 1113	10709				
18. 3432	10·961	615·81	83	27·36	27·474	28·952	1·478	9286	+ 1113	10399			10403	11·45
			16	—	14·336	15·796	1·460	9294	+ 1113	10407				
19. 3432	10·993	615·77	83	20·25	21·0895	22·494	1·4045	8818	+ 1113	9931			9919	9·04
			16	—	8·024	9·4065	1·3825	8795	+ 1113	9908				
20. 3432	11·042	615·74	83	16·88	17·032	18·408	1·376	8581	+ 1113	9694			9719	7·49
			16	—	4·026	5·392	1·366	8631	+ 1113	9744				
21. 2796 and 3000	11·172	614·01	83	14·50	14·8825	16·430	1·5475	9511	+ 87	9598			9559	6·655
22. 2796 and 3000	11·079	614·01	83	14·84	14·7765	16·2985	1·522	9433	+ 87	9520				
23. 3432	11·216	613·97	83	8·41	8·235	9·522	1·287	7879	+ 1113				8992	4·14
24. 2796 and 3000	10·726	613·95	83	7·63	4·1895	5·517	1·3275	8498	+ 87				8585	2·615

TABLE VI.—*Heat of Dissolution of Hexhydrated Potassium Magnesium*

Sample.	w.	W.	Therm.	τ.	t.		t'.
1. 3433	15·340	612·28	81	36·74	37·272		35·7375
2. 2789	14·865	612·15	81	31·08	32·148		30·618
3. 2789	14·481	612·04	81	31·66	32·284		30·7955
4. 2775	14·731	613·87	81	29·15	29·542	(21·26)	28·019
			16	—	39·786		38·2725
5. 3433	15·086	613·87	81	28·84	28·8435	(21·01)	27·277
			16	—	39·089		37·5285
6. 3433	14·607	613·72	81	24·76	24·856		23·3425
			16	—	35·127		33·591
7. 2789	15·214	611·16	81	23·49	23·157		21·579
8. 2789	14·876	612·05	81	20·63	20·642	(17·82)	19·085
9. 3433	15·074	613·82	81	20·10	20·279	(17·70)	18·712
			16	—	30·532		28·942
10. 3433	15·032	613·79	81	15·93	16·488		14·870
			16	—	26·723		25·090
11. 2789	14·843	611·00	81	14·97	15·133		13·514
12. 2775	15·834	611·00	81	14·87	15·132		13·526
13. 2789	15·028	613·77	81	13·21	13·613	(15·125)	11·9785
			16	—	23·8125		22·166
14. 2789	14·919	612·00	81	13·72	13·161	(14·93)	11·511
15. 2789	14·350	611·85	81	13·16	13·058		11·4825
16. 3433	14·608	613·65	81	12·10	13·054	(14·91)	11·443
			16	—	23·2495		21·627
17. 3433	14·873	613·68	83	36·19	36·631	(14·94)	34·980
			16	—	23·397		21·7685
18. 3433	15·282	613·78	83	32·08	31·644		29·917
			16	—	18·464		16·7785
19. 3433	14·768	613·62	83	27·51	27·509		25·8175
			16	—	14·371		12·7235
20. 2789	14·871	611·83	83	23·80	23·9175		22·182
21. 3433	15·403	613·75	83	20·06	20·954		19·138
			16	—	7·8885		6·0935
22. 3433	14·708	613·54	83	16·50	17·033		15·262
			16	—	4·024		2·258
23. 2789	14·989	611·88	83	13·25	13·6465	(6·19)	11·826
24. 2789	15·029	612·14	83	13·69	13·7155		11·8815
25. 3433	15·318	611·96	83	12·88	12·606	(5·81)	10·7355
26. 3433	15·238	611·91	83	8·13	8·014		6·144
27. 2789	14·934	611·80	83	7·45	3·771		1·915

Sulphate. $MgSO_4,K_2SO_4,6H_2O = 401{\cdot}40$; $\frac{3}{80}$ *mol.* = 15·053 *grams.*

$t - t'$.	*m.*				$6l_m$.	M.	T.
1·5345				−9512	−9803	+ 291	24°·25 C.
1·530	−9788			−9777	−9700	− 77	22·29
1·4885	−9769						
1·523	−9849	−9804		−9835	−9645	− 190	21·13
1·5135	−9759						
1·5665	−9900	−9867					
1·5605	−9833						
1·5135	−9875			−9935	−9554	− 381	19·47
1·536	−9994						
1·578				−9851	−9522	− 329	18·82
1·557	−9951	−9968		−9962	−9468	− 494	17·74
1·567	−9910						
1·590	−10026						
1·618	−10261			−10293	−9389	− 904	16·24
1·633	−10325						
1·619	−10353			−10314	−9364	− 950	15·725
1·606	−10274						
1·6345	−10371	−10394		−10452	−9328	−1124	15·00
1·6465	−10417						
1·650	−10515	−10490					
1·5755	(−10454)						
1·611	−10511	−10533	−10470				
1·6225	−10554						
1·651	−10411	−10408					
1·6285	−10405						
1·727	−10601			−10542	−9227	−1315	13·05
1·6855	−10483						
1·6915	−10741			−10670	−9145	−1525	11·46
1·6475	−10600						
1·7355				−10917	−9076	−1841	10·12
1·816	−11059			−11067	−9019	−2048	9·00
1·795	−11076						
1·771	−11291			−11349	−8941	−2408	7·49
1·766	−11408						
1·8205	−11363	−11393		−11411	−8867	−2544	6·06
1·834	−11422						
1·8705	−11447						
1·870				−11476	−8854	−2705	4·06
1·896				−11845	−8726	−3149	2·45

TABLE VII.—*Heat of Dissolution of Anhydrous Potassium Copper Sulphate.* $CuSO_4,K_2SO_4 = 333{\cdot}02$; $\frac{3}{80}$ *mol.* = 12·488 *grams.*

Sample.	*w.*	W.	Therm.	*τ.*	*t.*	*t′.*	*t′ − t.*	M.			T.
1. 2744, 2746, and 2717	12·518	614·271	81	33·60	33·814	35·414	1·600		10109	10100	22°·90 C.
2. 2744, &c...	12·494	614·271	81	35·18	33·737	35·331	1·594		10091		
3. 2717	12·392	614·12	81	18·62	21·456	22·988	1·532	9753	9665		
4. 2717	12·434	614·12	81	18·52	21·3845	22·8905	1·506	9577			
5. 2744	12·588	614·12	81	20·35	21·397	22·948	1·551	9743	9762	9709	18·25
6. 2744	12·605	614·21	81	26·54	21·7795	23·3385	1·559	9781			
7. 2746	12·423	614·21	81	25·94	21·705	23·222	1·517		9657		
8. 2744, &c...	12·471	614·21	81	21·65	22·3735	23·910	1·5365		9741		
9. 2744	12·570	614·02	83	34·32	32·163	33·636	1·473		9116		
10. 2746	12·611	614·02	83	34·18	32·1275	33·602	1·4745		9096	9094	13·25
11. 3426	12·320	614·12	83	32·02	32·251	33·678	1·427		9070		
12. 2744, &c...	12·385	614·05	83	20·92	20·815 (8·94)	22·1095	1·2945		8132	8146	8·60
13. 3426	12·141	614·03	83	18·99	18·9385 (8·21)	20·2135	1·275		8160		
14. 3426	12·043	614·00	83	13·25	13·275 (6·05)	14·4565	1·1815		7621	7637	6·03
15. 2744, &c...	12·473	614·00	83	14·31	13·109 (6·01)	14·336	1·227		7653		
16. 3426	12·788	614·07	83	9·02	8·1375	9·323	1·1855			7210	4·11
17. 2744, &c...	12·364	613·95	83	1·57	4·1195	5·199	1·0795			6789	2·59

TABLE VIII.—*Heat of Dissolution of Hexhydrated Potassium Copper Sulphate.* $CuSO_4,K_2SO_4,6H_2O = 440{\cdot}78$; $\frac{3}{80}$ *mol.* $= 16{\cdot}529$ *grams.*

Sample.	w.	W.	Therm.	τ.	t.	t′.	t − t′.	m.			$6l_m$.	M.	T.
1. 2738	16·038	612·04	81	31·57	33·712	31·6295	2·0825	−13544		−13591	−9733	−3858	22°·91C.
2. 2738	15·687	611·96	81	32·63	33·9025	31·851	2·0515	−13639					
3. 2738	15·975	612·01	81	27·43	27·619	25·531	2·088			−13632	−9611	−4021	20·53
4. 2693	16·500	612·04	81	20·10	23·191 (18·82)	21·012	2·179	−13774	−13735				
5. 2693	16·372	612·04	81	20·61	23·128	20·978	2·150	−13697					
6. 2738	16·522	612·04	81	17·40	23·062 (18·83)	20·852	2·190	−13825	−13852	−13728	−9516	−4212	18·71
7. 2738	16·454	612·04	81	17·92	23·353	21·1635	2·1895	−13879					
8. 2738	16·044	611·99	81	23·31	21·7155 (18·25)	19·6445	2·071		−13463				
9. 2738	10·738	609·65	81	15·11	13·707	12·226	1·441			−13942	−9334	−4608	15·15
10. 2738	16·448	611·92	83	32·50	34·124	31·850	2·274	−14220					
11. 2738	16·536	611·94	83	33·50	33·988	31·713	2·275	−14118		−14154	−9274	−4880	13·965
12. 2738	15·889	611·96	83	34·36	33·949	21·762	2·187	−14125					
13. 2738	15·697	611·82	83	31·05	30·561	28·4035	2·1575			−14102	−9205	−4897	12·63
14. 2738	16·261	611·88	83	23·05	20·943	18·6475	2·296	−14488		−14499	−9019	−5480	9·00
15. 2738	16·108	611·84	83	23·13	20·935	18·657	2·278	−14511					
16. 2738	16·336	611·85	83	16·52	13·084	10·724	2·360			−14796	−8854	−5942	5·99
17. 2738	16·029	611·73	83	1·16	3·0475	0·638	2·409			−15418	−8657	−6761	2·17

TABLE IX.—*Heat of Dissolution of Anhydrous Sodium Sulphate.* $Na_2SO_4 = 141{\cdot}81$; $\frac{3}{40}$ *mol.* $= 10{\cdot}636$ *grams.*

Sample.	*w.*	W.	Therm.	*τ.*	*t.*	*t′.*	*t′ − t* or *t − t′.*	M.			T.
1. 2775	10·668	614·32	81	38·41	38·396	38·4795	0·0835	264		276	24·66°C.
2. 2775	10·601	614·32	81	39·79	38·252	38·3435	0·0905	287			
3. 3604	10·603	608·39	39	36·13	38·634	38·976	0·342	169		175	22·13
4. 3604	10·659	608·39	39	39·37	39·3625	39·732	0·3695	180			
5. 2775	10·550	614·25	81	25·3	27·626	27·647	0·021	68		57	20·55
6. 3036	10·653	614·25	81	27·14	27·658	27·674	0·016	47			
7. 3052	10·627	614·25	81	27·51	27·325	27·342	0·017	50			
8. 3081	10·481	614·25	81	31·33	27·670	27·689	0·019	61			
9. 3604	10·617	608·33	39	52·73	51·900 (18·64)	51·708	0·192	− 94		−71	18·617
10. 3604	10·605	608·33	39	51·65	52·290	52·12	0·170	− 83			
11. 3604	10·641	608·33	39	37·64	42 750 (18·57)	42·679	0·071	− 35			
12. 3604	10·591	608·32	39	42·87	44·395	44·225	0·170	− 83		−88	17·76
13. 3604	10·611	608·32	39	41·44	44·106	43·915	0·191	− 93			
14. 3604	10·574	608·32	39	39·50	38·866 (16·42)	38·3845	0·4815	−237		−232	16·307
15. 3604	10·611	608·32	39	43·77	41·420 (16·20)	40·958	0·462	−226			
16. 2775	10·550	614·16	83	35·75	36·9915	36·909	0·0825	−259		−278	15·07
17. 3052	10·685	614·16	83	36·06	36·871	36·775	0·096	−298			
18. 3604	10·537	608·27	39	44·08	43·0315 (14·51)	42·3965	0·635	−313		−314	14·34
19. 3604	10·613	608·27	39	54·24	55·666 (14·17)	55·023	0·643	−315			
20. 3604	10·558	608·24	39	29·25	49·0775	48·0555	1·022	−501	−502	−494	12·215
21. 3604	10·555	608·24	39	29·41	49·705	48·685	1·020	−502			
22. 3604	10·616	608·24	39	48·84	50·168	49·176	0·992		−486		
23. 3604	10·460	608·20	39	34·21	34·841 (10·34)	32·525	1·316	−654	−655	−678	10·00
24. 3604	10·309	608·20	39	36·09	35·0975	33·7965	1·301	−656			
25. 3052	10·658	614·08	83	21·62	23·456	23·240	0·216	−671	−684		
26. 3052	10·524	614·08	83	24·26	23·421 (9·94)	23·198	0·222	−698			
27. 3407	10·451	614·08	83	23·97	23·485	23·270	0·215	−682			
28. 3098	10·503	614·07	83	22·63	22·295 (9·5)	22·071	0·224		−707		

TABLE IX—(*continued.*)

Sample.	$w.$	W.	Therm.	$\tau.$	$t.$		$t'.$	$t-t'.$	M.			T.
29. 3604	10·670	608·18	39	43·21	42·154	(8·70)	40·450	1·704		−830		
30. 3604	10·619	608·18	39	51·04	51·379	(8·32)	49·615	1·764	−863		−848	8°·437 C.
31. 3604	10·582	608·18	39	51·98	51·539		49·805	1·734	−851	−857		
32. 3407	10·483	614·00	83	8·20	12·828	(5·95)	12·505	0·323	−1021	−1016		
33. 3407	10·588	614·00	83	9·87	12·803		12·480	0·323	−1011			
34. 3604	10·554	608·14	39	58·64	50·672	(5·92)	48·550	2·122		−1045	−1039	5·871
35. 3604	10·651	608·14	39	59·60	46·673	(5·665)	44·466	2·207		−1077		
36. 3604	10·696	608·11	39	55·30	53·612		51·152	2·4602			−1195	4·07
37. 3407	10·443	613·95	83	5·47	5·325	(3·03)	4·9295	0·3955	−1254		−1324	2·68
38. 3407	10·100	613·95	83	1·42	3·467	(2·33)	3·042	0·425	−1394			

TABLE X.—*Heat of Dissolution of Decahydrated Sodium Sulphate.* $Na_2SO_4,10H_2O = 321·41$; $\frac{3}{40}$ *mol.* $= 24·106$ *grams.*

Sample.	$w.$	W.	Therm.	$\tau.$	$t.$		$t'.$	$t-t'.$	$m.$			$10l_m.$	M.	T.
1. 3095	23·974	623·53	81	38·76	39·191		33·264	5·927			−19156	−16400	−2756	25°·015 C.
2. 3418	23·967	621·59	81	36·86	37·400		31·459	5·941			−19147	−16345	−2802	24·31
3. 3095	24·087	623·47	81	34·76	34·306	(23·07)	28·3335	5·9725	−19211	−19125				
4. 3095	23·899	623·24	81	34·57	34·349		28·474	5·875	−19039		−19138	−16234	−2902	23·10
5. 3418	23·816	621·46	81	34·56	34·191	(23·11)	28·291	5·900	−19132	−19145				
6. 3418	24·121	621·53	81	34·30	34·247		28·264	5·983	−19158					
7. 3095	23·908	623·21	81	28·38	28·113	(20·76)	22·188	5·925	−19193	−19173				
8. 3095	24·052	623·50	81	28·48	28·2905		22·3445	5·946	−19154					
9. 3418	23·698	623·05	81	28·27	28·045	(20·7)	22·180	5·865	−19194		−19156	−16033	−3123	20·715
			16	—	33·290		32·410	5·880	−19190					
10. 3418	24·057	623·28	81	28·47	28·082	(20·7)	22·1545	5·9275	−19116	−19147				
			16	—	38·3355		32·401	5·9345	−19086					

TABLE X—(*continued.*)

Sample.	w.	W.	Therm.	τ.	t.	t'.	$t-t'$.	m.			$10l_m$.	M.	T.
11. 3418	24·002	623·44	81	24·62	24·698	18·788	5·910	−19077		−19104	−15920	−3184	19°·41 C.
			16	—	34·944	29·010	5·944	−19130					
12. 3095	24·365	621·72	81	22·35	22·3665	16·314	6·0425			−19160	−15842	−3318	18·515
13. 3418	23·855	623·16	81	21·30	21·266	15·375	5·891	−19156					
			16	—	31·4885	25·582	5·9065	−19153		−19158	−15807	−3351	18·08
14. 3418	23·922	623·19	81	21·37	21·300	15·390	5·910	−19164					
			16	—	31·524	25·599	5·925	−19160					
15. 3418	23·965	623·19	81	18·80	18·695	12·769	5·926	−19182					
			16	—	28·899	22·9885	5·9105	−19079		−19131	−15724	−3407	17·11
16. 3418	24·061	623·26	81	18·80	18·7575	12·8195	5·938	−19138					
			16	—	28·9575	23·0065	5·951	−19126					
17. 3418	23·795	623·10	81	17·15	17·147	11·272	5·875	−19150					
			16	—	27·366	21·462	5·904	−19192		−19187	−15669	−3518	16·50
18. 3418	24·377	623·43	81	17·06	17·1915	11·163	6·0285	−19191					
			16	—	27·4035	21·3515	6·052	−19213					
19. 3418	24·090	623·31	81	15·98	15·6445	9·706	5·9385	−19126					
			16	—	25·857	19·891	5·966	−19162		−19137	−15623	−3514	15·94
20. 3418	24·055	623·22	81	15·65	15·742	9·8195	5·9225	−19100					
			16	—	25·961	20·0055	5·9555	−19153					
21. 3418	24·239	623·29	83	36·09	33·185	30·099	6·087	−19178					
			16	—	22·950	16·9435	6·0065	−19170		−19121	−15522	−3599	14·76
22. 3418	24·359	623·35	83	36·32	36·111	30·025	6·085	−19076					
			16	—	22·874	16·871	6·003	−19060					
23. 3095	24·236	623·28	83	32·58	32·418 (13·39)	26·345	6·073	−19098	−19075				
24. 3095	23·778	623·35	83	32·70	32·624	26·6805	5·9435	−19053					
25. 3418	24·150	623·21	83	33·43	32·4465 (13·36)	26·3865	6·060	−19164		−19113	−15404	−3709	13·365
			16	—	19·250	13·287	5·963	−19102	−19125				
26. 3418	24·269	623·29	83	33·31	32·548 (13·36)	26·4715	6·0765	−19124					
			16	—	19·300	13·365	5·995	−19112					

TABLE X.—(*continued.*)

Sample.	w.	W.	Therm.	τ.	t.		t'.	$t-t'$.	m.			$10l_m$.	M.	T.
27. 3418	24·160	623·09	83	28·79	29·573		23·545	6·028	−19001		−19098	−15309	−3789	12°·25 C.
			16	—	16·4355		10·4255	6·010	−19198					
28. 3418	24·475	623·37	83	26·81	26·3845		20·260	6·1245	−19115		−19050	−15206	−3844	11·03
			16	—	13·2615		7·228	6·0335	−19076					
29. 3418	23·861	623·02	83	26·76	26·3345		20·4275	5·907	(−18900)					
			16	—	13·2210		7·3535	5·8675	−19018					
30. 3418	24·012	623·09	83	26·61	24·676		18·700	5·976	−19003		−19003	−15150	−3853	10·40
			16	—	11·584		5·6685	5·899	−19002					
31. 3418	23·937	623·04	83	23·23	23·2365		17·2855	6·001	−19170		−19134	−15108	−4026	9·88
			16	—	10·189		4·252	5·937	−19182					
32. 3418	24·349	623·27	83	23·18	23·3765		17·2825	6·094	−19116					
			16	—	10·279		4·2785	6·0005	−19067					
33. 3095	24·017	623·21	83	22·45	22·002	(9·59)	15·986	6·016	−19140		−19115	−15076	−4039	9·54
34. 3095	23·910	623·16	83	22·70	22·740	(9·39)	16·734	6·006	−19090					
35. 3418	24·249	623·20	83	20·34	20·597		14·5045	6·0925	−19185		−19141	−15025	−4116	8·85
			16	—	7·5245		1·5185	6·006	−19157					
36. 3418	24·502	623·34	83	20·78	20·582		14·467	6·115	−19064					
			16	—	7·5155		1·449	6·0665	−19158					
37. 3418	24·495	623·33	83	17·30	18·9745		12·814	6·1605	−19211		−19204	−14966	−4238	8·25
			16	—	5·944		−0·144	6·088	−19231					
38. 3418	24·565	623·37	83	17·37	19·1585		13·0025	6·156	−19143					
			16	—	6·1295		0·024	6·1055	−19232					
39. 3095	24·269	621·44	83	11·1	11·322	(5·3)	5·2885	6·033	−18892	−18902	−18926	−14736	−4190	5·55
40. 3095	23·829	623·15	83	11·45	11·8805	(5·54)	5·9665	5·914	−18912					
41. 3418	24·127	621·48	83	14·99	15·2545	(6·815)	9·2035	6·050	−19056					
42. 3418	23·842	621·19	83	11·99	12·065	(5·62)	6·123	5·942	−18930	−18938				
43. 3418	24·227	621·41	83	12·54	12·1865		6·1455	6·041	−18947					
44. 3418	22·802	620·61	83	9·26	9·372	(4·58)	3·683	5·689	−18934					
45. 3418	24·637	621·62	83	6·43	6·580		0·445	6·135	−18928		−18928	−14553	−4375	3·53
46. 3418	24·417	621·49	83	6·81	6·735		0·654	6·081	−18927					

TABLE XI.—*Heat of Dissolution of Potassium Sulphate.* $K_2SO_4 = 173 \cdot 88$; $\frac{3}{40}$ *mol.* = 13·041 *grams.*

Sample.	*w*.	W.	Therm.	τ.	*t*.		*t'*.	*t* − *t'*.	M.	Correction.	M corrected.				T.
1. 3603	13·097	610·14	80*	—	30·935		29·117	1·818	—	—	−5851			−5841	26°·50C.
			84*	29·77	29·813		28·795	1·018	—	—	−5831				
2. 3603	13·108	610·08	80	39·48	39·309	(25·42)	34·426	1·883	—	—	−6055	−5972			
			84	—	34·545		33·517	1·028	—	—	−5889				
3. 3613	13·525	608·45	39	52·94	52·565	(25·35)	39·835	12·730	−6010	−63	−5947				
4. 3428	12·950	608·45	39	52·56	52·5665	(25·27)	40·421	12·1455	−5989	−38	−5951	−5952		−5948	25·21
5. 3428	13·126	608·45	39	52·14	52·3125		39·977	12·3155	−5991	−38	−5953				
6. 3603	13·182	610·07	80	38·24	38·3215		36·4715	1·850	—	—	−5915				
			84	—	34·018		32·975	1·043	—	—	−5941				
7. 3603	13·027	610·07	80	38·34	38·3265	(25·04)	36·5005	1·826	—	—	−5908	−5934			
			84	—	34·023		32·987	1·036	—	—	−5971				
8. 3603	13·194	610·09	80	36·65	36·142		34·267	1·875	—	—	−5990				
			84	—	32·784		31·741	1·043	—	—	−5936	−5955			
9. 3603	13·123	610·09	80	36·80	36·145		34·289	1·856	—	—	−5961				
			84	—	34·289		31·752	1·037	—	—	−5933			−6011	24·2
10. 3603	13·162	610·09	80*	—	25·640		23·760	1·880	—	—	−6020				
			84*	26·81	26·848		25·778	1·070	—	—	−6104				
11. 3603	13·123	610·09	80*	25·85	25·454		23·5545	1·8995	—	—	−6101	−6067			
			84	—	32·829		31·773	1·056	—	—	−6042				
12. 3603	13·088	608·40	39	52·64	51·8855		39·244	12·6415	—	—	−6163				
13. 3428	13·435	608·40	39	53·42	52·7225	(22·90)	39·810	12·9125	−6139	−38	−6131	−6137			
14. 3613	13·049	608·40	39	52·40	52·012		39·412	12·570	−6150	−63	−6087			−6150	22·865
15. 3603	13·172	610·04	80	32·93	32·677		30·742	1·935	—	—	−6191				
			84	—	30·818		29·733	1·085	—	—	−6181	−6163			
16. 3603	12·873	610·04	80	32·90	32·735	(22·87)	30·864	1·871	—	—	−6126				
			84	—	30·853		29·798	1·055	—	—	−6153				

* Some of the mercury having been removed into the upper chamber.

TABLE XI—(*continued*).

Sample.	w.	W.	Therm.	r.	t.		t'.	$t-t'$.	M.	Correction.	M corrected.			T.
17. 3428	12·976	609·88	16	39·44	39·189		37·1965	1·9925	−6288	−38	−6250		−6267	21°·10 C.
			80	—	28·1695		26·227	1·9425	−6322	−38	−6284			
18. 3603	13·132	610·00	80	27·02	26·213		24·242	1·971	—	—	−6325		−6335	20·31
			84	—	27·204		26·094	1·110	—	—	−6346			
19. 2725	13·016	607·99	81	22·4	23·811	(19·06)	21·7555	2·0555	−6466	+18	−6484			
20. 3428	13·005	609·85	16	—	33·846	(19·015)	31·789	2·057	−6477	−38	−6439	−6472		
			80	23·51	22·9785		20·959	2·0195	−6542	−38	−6504			
21. 3603	13·184	609·82	16	33·68	33·8825		31·806	2·0765	—	—	−6449			
			84	—	25·410	(18·93)	24·287	1·123	—	—	−6393	−6431	−6467	18·912
22. 3603	12·920	609·82	84	—	25·420		24·318	1·102	—	—	−6403			
			80	22·97	23·045		21·059	1·986	—	—	−6478			
23. 2725	13·127	607·99	81	19·62	23·154	(18·8)	21·086	2·068	−6516	+18		−6534		
24. 3603	13·021	608·33	39	31·39	52·0635	(18·6)	38·7685	13·295	—	—		−6518		
25. 3428	12·909	609·82	16	29·19	29·0835	(17·19)	27·003	2·0805	−6599	−38	−6561	−6561		
			80	—	18·349		16·326	2·023	−6600	−38	−6562		−6607	16·915
26. 3428	12·791	609·81	16	27·24	27·635	(16·64)	25·542	2·093	−6700	−38	−6662	−6653		
			80	—	16·940		14·916	2·024	−6682	−38	−6644			
27. 3603	13·038	609·92	80	14·88	13·789		11·695	2·094	—	—	−6767	−6820		
			84	—	20·230		19·036	1·194	—	—	−6874		−6792	15·42
28. 3603	13·009	609·92	80	14·7	813·855		11·783	2·072	—	—	−6711	−6764		
			84	—	20·269		19·088	1·181	—	—	−6816			
29. 3603	12·955	608·28	39	51·9	352·290	(15·03)	38·450	13·840	—	—		−6820		
30. 2725	12·908	607·90	16	22·6	722·890		20·7275	2·1625	−6822	+18	−6840		−6833	14·895
31. 2725	13·015	609·78	16	22·8	123·0425	(14·85)	20·8615	2·181	−6861	+18	−6879	−6836		
			80	—	12·497		10·405	2·092	−6771	+18	−6789			

TABLE XI—(*continued.*)

Sample.	w.	W.	Therm.	τ.	t.	t'.	$t - t'$.	M.	Correction.	M corrected.				T.
32. 3603	13·071	608·26	39	53·42	52·457 (13·96)	38·2945	14·1625	—	—	−6921	−6928			
33. 3603	13·135	608·26	39	52·10	52·3035 (13·95)	38·0325	14·270	—	—	−6936				
34. 3428	13·160	608·26	39	49·95	52·0265	37·6645	14·362	−6966	−38		−6928	−6941		
35. 2725	13·104	608·26	39	52·78	52·088 (13·96)	37·823	14·265	−6949	+18		−6967		−6952	13°·946 C.
36. 2725	13·106	607·89	83	34·36	33·825	31·536	2·289	−7032	+18	−7050	−6979			
37. 2725	13·213	607·89	83	35·18	34·1375 (13·935)	31·8775	2·260	−6890	+18	−6908				
38. 2725	13·052	607·89	83	35·67	33·9725	31·7155	2·257	−6967	+18		−6985	−6963		
39. 2725	13·158	607·89	83	34·15	33·9815	31·7225	2·259	−6918	+18		−6936			
40. 3603	13·035	608·24	39	51·55	52·476	38·135	14·341	—	—				−7023	12·36
41. 2725	13·107	607·90	83	25·39	25·377 (10·75)	23·062	2·315	−7115	+18		−7133			
42. 3603	12·889	608·20	39	52·18	52·380 (10·455)	37·820	14·50	—	—		−7210		−7180	10·434
43. 3428	12·98	607·92	83	24·34	24·530	22·193	2·337	−7253	−38	−7215				
44. 3428	13·092	607·92	83	24·42	24·491 (10·35)	22·145	2·346	−7219	−38	−7181	−7184			
45. 3428	12·978	607·92	83	24·35	24·515	22·197	2·318	−7195	−38	−7157				
46. 3428	13·062	607·92	83	24·37	24·515	22·173	2·342	−7223	−38	−7185				
47. 2725	13·014	607·91	83	23·05	23·034	20·694	2·340	−7243	+18	−7261			−7233	9·82
48. 2725	13·163	607·91	83	23·06	23·212	20·8635	2·3485	−7187	+18	−7205				
49. 3603	12·987	608·18	39	52·02	52·905	37·770	15·135	—	—				−7438	8·33
50. 2725	13·193	607·87	83	14·98	14·791 (6·63)	12·3185	2·4725	−7549	+18	−7567	−7576			
51. 2725	13·038	607·87	83	15·12	14·726	12·268	2·458	−7568	+18	−7586			−7600	6·57
52. 3613	13·048	608·15	39	52·01	52·447 (6·45)	36·682	15·756	−7711	−63		−7648			
53. 3603	13·051	608·14	39	60·90	51·438 (5·965)	35·708	15·730	—	—		−7692		−7672	5·855
54. 3428	12·823	607·85	83	11·52	11·495 (5·80)	9·0085	2·4505	−7698	−38	−7660	−7662			
55. 3428	12·995	607·85	83	11·79	11·6125	9·1275	2·485	−7703	−38	−7665				
56. 3613	13·046	608·11	39	51·44	52·3445 (3·99)	36·0445	16·300	−7974	−63		−7911			
57. 2725	13·068	607·81	83	6·63	5·2205 (3·01)	2·6595	2·5610	−7894	+18		−7912		−7925	3·14
58. 2725	12·992	607·81	83	2·50	3·706 (2·42)	1·1465	2·5595	−7945	+18		−7953			

TABLE XII.—*Heat of Dissolution of Anhydrous Lithium Sulphate.* $Li_2SO_4 = 109 \cdot 84$; $\frac{3}{40}$ *mol.* $= 8 \cdot 238$ *grams.*

Sample.	*w.*	W.	Therm.	τ.	*t.*	*t'.*	*t' − t.*	M.	Correction.	M corrected.		T.
1. 3074	8·205	614·27	81	32·92	33·688	35·746	2·058	—	—		6541	22°·86C.
2. 3406	8·396	614·26	81	30·54	30·477	32·593	2·116	—	—		6574	21·64
3. 3093	8·230	614·21	81	22·36	21·752	23·782	2·030	6434	−81		6353	18·27
4. 3406	8·165	614·20	81	20·29	20·220	22·190	1·970	—	—		6293	17·68
5. 3086	8·294	614·11	83	32·09	31·576 (13·02)	33·557	1·981	—	—	6130	6117	13·43
6. 3406	8·146	614·11	83	33·61	33·732 (13·85)	35·670	1·938	—	—	6105		
7. 3086	8·145	614·05	83	21·38	22·342	24·161	1·819	—	—	5731	5728	9·50
8. 3406	8·304	614·05	83	23·60	22·252	24·105	1·853	—	—	5726		
9. 3086	8·197	614·00	83	14·19	13·551	15·312	1·761	—	—	5512		
10. 3093	8·274	614·00	83	13·94	13·454	15·255	1·801	5585	−81	5504	5506	6·14
11. 3406	8·207	614·00	83	13·22	13·467	15·227	1·760	—	—	5503		
12. 3406	8·328	613·95	83	1·87	2·359	4·006	1·647	—	—		5074	1·91

TABLE XIII.—*Heat of Dissolution of the Monohydrated Sulphates of Copper, Magnesium, and Lithium.*

$$CuSO_4,H_2O = 176\cdot80;\ \frac{3}{40}\ mol. = 13\cdot260\ grams.$$
$$MgSO_4,H_2O = 137\cdot72\quad ,, \quad = 10\cdot329\quad ,,$$
$$Li_2SO_4,H_2O = 127\cdot80\quad ,, \quad = 9\cdot585\quad ,,$$

Sample.	w.	W.	Therm.	τ.	t.	t'.	$t' - t$.	m.		l_m.	M.	T.
$CuSO_4,H_2O$.												
1. 2734	13·305	614·27	81	34·74	33·739	36·621	2·882	9115	9089	1622	10711	22°·88C.
2. 2734	13·428	614·27	81	34·74	33·739	36·631	2·892	9063				
3. 2734	13·272	614·47	81	19·26	20·625	23·440	2·815	8295	8892	1578	10470	17·83
4. 2734	13·387	614·47	81	19·75	20·714	23·533	2·819	8859				
5. 2734	13·297	615·37	83	34·85	31·589	34·384	2·795	8701	8710	1537	10247	13·00
6. 2734	13·480	615·39	83	34·54	31·484	34·323	2·839	8718				
$MgSO_4,H_2O$.												
7—15. 2755, 2758, 3032, and 3025 ..	For details see *Chem. Soc. J.*, Trans., 1885, 100.					—	—		12091	1617	13708	22·30
Li_2SO_4,H_2O.												
16. 3215	9·708	608·34	83	33·49	33·6195	34·6495	1·03		3138	1548	4686	13·80
17. 3353	10·926	610·66	83	32·82	31·4625	32·586	1·1235		2911	1537	4448	12·97

TABLE XIV.—*Heat developed on Mixing Solutions of Magnesium Sulphate or Copper Sulphate with a Solution of Potassium Sulphate.*

Strength of each solution = 1 molecule to 400 H_2O.
Quantity taken 307 c.c. of each.
Thermometers employed, 81 and 83.

A.—*Magnesium and Potassium Sulphates Mixed.*

Observed heat development.		Heat developed in blank experiments.		Corrected heat development.	Mean temperature.
1. + 56 cal. 2. + 24 „	+ 40 cal.		+ 63 cal.	− 23 cal.	7°·07 C.
3. + 72 „ 4. + 38 „	+ 55 „	+ 88 cal. + 38 „	+ 63 „	− 8 „	13·32 „
5. − 6 „ 6. − 22 „	− 14 „	− 35 „ 0 „	− 17 „	+ 3 „	23·0 „

B.—*Copper and Potassium Sulphates mixed.*

1. + 104 cal. 2. + 118 „	+ 111 cal.	+ 102 cal. + 112 „	+ 107 cal.	+ 4 cal.	10·6° C.
3. + 22 „ 4. + 51 „	+ 36 „		+ 38 „	− 2 „	13·22 „
5. − 19 „ 6. − 6 „	− 13 „	− 16 „ − 54 „	− 35 „	+ 22 „	22·89 „

XXX.—*Contributions to the History of Cyanuric Chloride and Cyanuric Acid.*

By ALFRED SENIER, M.D.

RECENT experiments on cyanuric acid and melamine have shown beyond much doubt that these substances are normal, and not iso in their constitution. Nevertheless, it seemed interesting to extend the data upon which this view rests by the preparation and study of other cyanuric derivatives. With this object, I have investigated the action of cyanuric chloride on the salts of various organic acids.

Sodium Acetate.—If this salt be heated with cyanuric chloride in a closed tube for eight hours at 100°, a reaction takes place, and on opening the tube the characteristic odour of acetyl chloride is perceived. By treating the contents of the tube with cold ether, the

acetyl chloride is readily dissolved, whilst any unchanged cyanuric chloride, being but sparingly soluble, remains for the greater part with the residue. By repeated washing with hot ether, the whole of the cyanuric chloride can be removed and a yellow residue is left, mostly sodium cyanurate. This when dissolved in water gives, on the addition of hydrochloric acid, a crystalline precipitate, which readily responds to the cuprammonium test for cyanuric acid.

The reaction, therefore, is quite different from what was expected. It was hoped that a triacetyl cyanurate would be formed thus :—

$$C_3N_3Cl_3 + 3C_2H_3O{\cdot}ONa = C_3N_3(O{\cdot}C_2H_3O)_3 + 3NaCl,$$

instead of which the following took place :—

$$C_3N_3Cl_3 + 3C_2H_3O{\cdot}ONa = C_3N_3(ONa)_3 + 3C_2H_3OCl.$$

By converting the acetyl chloride into acetic acid, and finally into silver acetate, the proportion formed was ascertained to be 22·5 per cent. of the theoretical yield.

Between silver acetate, in place of sodium acetate, and cyanuric chloride, no reaction was observed, and in the same manner cyanuric acid itself could not be induced to act on acetic anhydride.

Sodium Formate.—This salt behaves in a manner similar to the acetate. On opening the tube a gas is evolved, which on examination was found to be carbon monoxide, whilst the residue contains cyanuric acid in abundance. Apparently formyl chloride is produced in the first instance, immediately, however, breaking down into carbon monoxide and hydrochloric acid. The reaction is therefore—

$$C_3N_3Cl_3 + 3CHO{\cdot}ONa = C_3N_3(ONa)_3 + 3CO + 3HCl.$$

Sodium Benzoate.—In the benzoyl series, the same general reaction takes place, but whereas in the previous instances it was only partial, here 88 per cent. of the theoretical yield of benzoyl chloride is obtained. The reaction is expressed by the following equation :—

$$C_3N_3Cl_3 + 3C_7H_5O{\cdot}ONa = C_3N_3(ONa)_3 + 3C_7H_5OCl.$$

Action of Cyanuric Chloride on Benzamide.—In the hope of obtaining a benzoyl substituted melamine, cyanuric chloride and benzamide were heated in a closed tube for eight to ten hours at 100°. It was thought possible that instead of the desired action melamine and benzoyl chloride might be formed. But on opening the tube, there was a distinct odour of bitter almonds, and treatment with cold ether yielded abundance of an oily liquid having the character of benzonitrile, and easily converted into benzamide by treatment with concentrated sulphuric acid. The residue in the tube was almost pure cyanuric acid. The following action, therefore, had taken place :—

$$C_3N_3Cl_3 + 3C_6H_5{\cdot}CONH_2 = C_3N_3(OH)_3 + 3C_6H_5{\cdot}CN + 3HCl.$$

Notably, the cyanuric chloride, acting like phosphorus pentachloride, takes away water from the amide, leaving the nitrile, while it is itself resolved by the liberated water into cyanuric acid and hydrogen chloride.

Action of Benzoyl Chloride on Silver Cyanurate.—While I was engaged in these experiments, J. Ponomarew's "Zur Frage über die Constitution der Cyanursaure" appeared (*Ber.*, **18**, 3261), in which the author describes triacetyl cyanurate, one of the substances which I was seeking. It is obtained by the action of the acid chloride on silver cyanurate. By this elegant method, it seemed easy to prepare the other acid derivatives, and, in fact, it has already given me the corresponding tribenzoyl cyanurate.

Benzoyl chloride has no action on silver cyanurate in the cold, but by heating a mixture of the two in theoretical proportions, in closed tubes, for eight to ten hours at 100°, an action takes place, and on opening the tube much of the odour of the benzoyl chloride is found to have disappeared. The contents are extracted with boiling chloroform, which on evaporation gives a crystalline precipitate representing 25 to 30 per cent. of the theoretical yield. This recrystallised from chloroform, gives colourless needles of *tribenzoyl cyanurate*, $C_3N_3(OC_7H_5O)_3 = C_{24}H_{15}N_3O_6$, which requires—

	Theory.		Experiment.	
			I.	II.
C_{24}	288	65·31	65·32	—
H_{15}	15	3·40	3·86	—
N_3	42	9·52	—	10·23
O_6	96	21·77	—	—
	441	100·00		

The new compound shows no distinct melting point, being decomposed on heating. It is but sparingly soluble in chloroform, and insoluble in ether. By heating with water, it is converted into cyanuric and benzoic acids, this being effected very readily if the substance is enclosed in a tube with water and heated for a short time at 100°. This behaviour with water, which Ponomarew observed to occur in an analogous manner in the case of the acetyl-derivative, characterises this class of compound as mixed anhydrides.

In conclusion, I may mention that two experiments were instituted to obtain two cyanuric nuclei joined to each other. Cyanuric chloride was brought together, in closed tubes, with melamine, and also with silver cyanurate, but no reaction took place at temperatures from 100° to 250°.

University Laboratory,
Berlin, February, 1886.

XXXI.—*Contributions to a Knowledge of Cyanuric Derivatives.*

By Harold H. Fries.

By the action of ammonia on cyanuric chloride, Liebig (*Annalen*, **10**, 45) obtained chlorocyanamide, $C_3H_4N_5Cl$. The corresponding aniline compound was discovered soon afterwards by Laurent (*Ann. Chim. Phys.* [3], **22**, 97), and quite recently similar chlorine-derivatives have been obtained by various investigators, especially by A. W. Hofmann (*Ber.*, **18**, 2755) and Claësson (*Bihang till K. Svenska Vet. Akad. Handlingar*, Bd. **10**, No. 6), who acted on cyanuric chloride with amines. The final action of ammonia, or of the amines, on cyanuric chloride, is the production of simple or substituted melamines. Thus it is clear, as foreseen by the above-mentioned observers, that the compounds still retaining chlorine are intermediate derivatives between the trichloride on the one hand, and the melamine on the other. Take, for example, the methylamine series of substitutions :—

$(C \vdots N)_3Cl_3$. Cyanuric chloride.

$(C \vdots N)_3(NHCH_3)Cl_2$ $(C \vdots N)_3(NHCH_3)_2Cl$. Intermediate compounds.

$(C \vdots N)_3(NHCH_3)_3$. Trimethylmelamine.

All of these are known, with the exception of the first intermediate compound; this dichloro-derivative is also wanting in the other series which have hitherto been studied. The experiments with α-naphthylamine, which form the subject of this communication, have, however, given all these compounds. Similar results are to be expected in the case of β-naphthylamine, with the investigation of which I am at present engaged.

Primary α-Naphthylamido-cyanuric Chloride.—Solutions of cyanuric chloride and α-naphthylamine in dry ether are quickly mixed together in the proportion of 1 mol. of the chloride to 2 mols. of the α-naphthylamine.

A precipitate of α-naphthylamine hydrochloride occurs, which is removed by filtration, and the filtrate is evaporated to dryness. The residue crystallised several times from hot alcohol gives colourless needles of primary α-naphthylamido-cyanuric chloride,

$$(C \vdots N)_3(NH{\cdot}C_{10}H_7)Cl_2 = C_{13}H_8N_4Cl_2,$$

melting at 149°. The formula requires—

	Theory.		Experiment.			
C_{13}	156	53·61	53·47	—	—	—
H_8	8	2·75	3·01	—	—	—
N_4	56	19·24	—	19·05	18·94	—
Cl_2	71	24·40	—	—	—	24·44
	291	100·00				

Secondary α-Naphthylamido-cyanuric Chloride.—In this instance, the ethereal solutions are mixed slowly, drop by drop, and in the proportion of 4 mols. of α-naphthylamine to 1 mol. of cyanuric chloride. The precipitated α-naphthylamine hydrochloride is removed as before, and the residue, after evaporation, recrystallised several times from hot alcohol. In this way, colourless needles of secondary α-naphthylamido-cyanuric chloride, $(C \vdots N)_3(NHC_{10}H_7)_2Cl = C_{23}H_{16}N_5Cl$, are obtained, melting at 215°. This requires—

	Theory.		Experiment.		
C_{23}	276	69·43	69·32	—	—
H_{16}	16	4·02	4·25	—	—
N_5	70	17·60	—	17·51	—
Cl	35·5	8·95	—	—	9·21
	397·5	100·00			

The secondary compound is much more soluble in alcohol than the primary derivative, and by taking advantage of this fact they may be separated if they occur mixed together.

Tertiary α-Naphthylmelamine.—Tertiary α-naphthylmelamine is formed when either of the above compounds is heated for several hours at 100° in a closed tube, together with the theoretical proportion of α-naphthylamine. The melamine found is washed with alcohol and water, and recrystallised from chloroform. It melts at 223°, and has the formula $(C \vdots N)_3(NHC_{10}H_7)_3 = C_{33}H_{24}N_6$. This requires the following values:—

	Theory.		Experiment.		
C_{33}	396	78·57	78·33	—	—
H_{24}	24	4·76	4·90	—	—
N_6	84	16·67	—	16·67	16·85
	504	100·00			

Thus, in the case of α-naphthylamine, the whole series of derivatives theoretically possible are obtained, and there can be but little

doubt that the primary amido-compound can be prepared in the case of other amines, and with ammonia itself by working under suitable conditions.

University Laboratory,
Berlin.

XXXII.—*On the Essential Oil of Lime Leaves* (Citrus Limetta). Preliminary Notice.

By FRANCIS WATTS, F.C.S., Chemist to the Montserrat Company, Montserrat, W.I.

THE leaves and young shoots of the lime tree yield a fragrant yellow oil by distillation with water or in a current of steam. About 230 c.c. were prepared for the purposes of the present investigation.

The oil is moderately soluble in rectified spirit of wine, and has a sp. gr. = 0·8777 at 33° (water at 4° = 1). When agitated with soda solution, no appreciable diminution of volume was observed.

The oil was submitted to fractional distillation, and the several fractions were agitated with a strong solution of sodium bisulphite. It began to distil at about 170°, and the portion which passed over at this temperature did not combine with the bisulphite. It consisted of a hydrocarbon. On the other hand, the fraction obtained at 220—230° formed a crystalline mass with the bisulphite. But as this fraction had no action or but very slight action on silver nitrate, it was inferred that it consisted of a ketone rather than an aldehyde.

About one-third of the original oil boils at a temperature above 280°, has a viscid consistence, and exhibits a green fluorescence. It has, in fact, the appearance of colophene, and may possibly have been produced, at least in part, by the action of heat in the course of distillation.

From the lowest fractions, after digesting with sodium, a hydrocarbon was separated, boiling at 176—177°, inactive to polarised light, and having a refractive index at 30° of 1·4611 for red light. This compound unites with hydrogen chloride, forming a hydrochloride which melts at 49—50° in an atmosphere of hydrogen chloride. It also gives Riban's colour reaction with ferric chloride. Except with regard to its action on polarised light, this hydrocarbon resembles the citrenes.

From the action of sodium on the lower fractions of the original oil, and the production of a deep purple coloration when hydrogen

chloride is passed into them, the presence of terpinol is rendered very probable. It was not found possible to isolate it.

In order to determine the constitution of the ketone already referred to, it was oxidised by means of chromic mixture. Abundance of acetic acid was produced, and pelargonic acid was recognised by means of its copper salt. These facts, coupled with the boiling point (220—230°) of the compound, and the peculiar smell of pelargonium oil noticeable in some of the fractions, prove that the substance is methyl nonyl ketone, $CH_3 \cdot CO \cdot C_9H_{19}$.

The watery alkaline solution resulting from the first washing of the original oil was found to contain acetic acid, and the liquid submitted to distillation smelt strongly of amylic acetate. The quantity of this compound was, however, too small to admit of its separation.

From these results, it would appear that the principal constituents of the oil of lime leaves are, a citrene (b. p. 176° *circa*), terpinol ($C_{10}H_{17} \cdot OH$), methyl nonyl ketone, and a colophene.

XXXIII.—*The Formation of Acids from Aldehydes by the Action of Anhydrides and Salts, and the Formation of Ketones from the Compounds resulting from the Union of Anhydrides and Salts.*

By W. H. PERKIN, Ph.D., F.R.S.

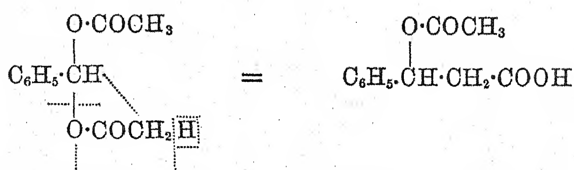
THE reactions which take place when aldehydes are heated with anhydrides and salts of fatty or bibasic acids, an account of which I had the honour of bringing under the notice of this Society some years since, have caused much work to be done with the object of obtaining a clearer insight into the way in which they take place. Fittig and his pupils, especially, have paid much attention to this subject, and this has resulted in the discovery of many very interesting products, and furnished us with fresh information respecting the reaction itself.

Since I brought this subject before the Society, much knowledge has been obtained in reference to the formation of condensation products, and it has been shown that the first phase of the reaction is, in very many cases at least, analogous to that of the formation of aldol from aldehyde discovered by Würtz in 1873; the splitting off of water being a second result. Fittig has shown that a change of a similar kind takes place in the formation of the unsaturated acids which are produced by this reaction, and that their formation is preceded by that of hydroxy-acids or their derivatives containing acid radicals, or of lactonic acids.

In my experiments, I was led to conclude that, in this reaction, condensation takes place between the aldehyde and anhydride, and Tiemann and Kraaz (*Ber.*, **15**, 2061) who, have worked a good deal on the subject, are of the same opinion. Fittig and others, however, consider that this is not the case, but that the condensation takes place between the aldehyde and the salt. As the evidence they give in support of this view does not appear to me to be conclusive, I have taken up the subject again. My experiments, however, are not yet completed, but as they have led to some new results which I desire to lay before the Society, I have ventured to refer to some of them, and to briefly consider their bearing. A very important point in the discussion of this matter is the double decomposition which may take place on heating the anhydride of one acid with the salt of another acid: results have been obtained in reference to this subject, but the work is still incomplete. I may state, however, that when sodium isobutyrate is boiled with acetic anhydride, the compound of sodium acetate and acetic anhydride I described some years since (*Chem. Soc. J.*, 1868, **21**, 185) is formed, and therefore there can be no doubt about double decomposition taking place in this instance. This is corroborated by Fittig and Otto (*Annalen*, **227**, 79), who show by their experiments that this takes place even at 100°. Sodium succinate when boiled with acetic anhydride was also found to form the compound of sodium acetate and acetic anhydride, and succinic anhydride was obtained from the mother-liquors.

In a former paper on the subject of this reaction, I referred to the fact that benzaldehyde with acetic anhydride yielded *benzylidene diacetate*, and said: "It is possible that the formation of this substance precedes that of the acid," meaning cinnamic acid (*Chem. Soc. J.*, 1877, i, 425), and I am still inclined to believe that this is the case, and that in the formation of other acids also, analogous products are first produced from the aldehydes.

There is the remarkable circumstance in connection with the formation of cinnamic acid, that the compound which (judging from Fittig's results) is the first product of the reaction, *i.e.*, acetylphenyllactic acid, has the same composition as benzylidene diacetate, only a slight intramolecular rearrangement of the latter substance being necessary for its formation:—



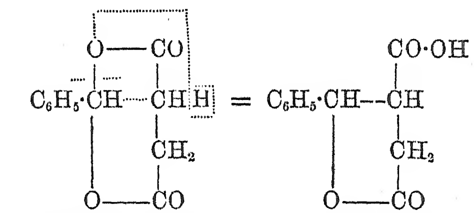
Benzylidene diacetate. Acetylphenyllactic acid.

This acid, as shown by the experiment of Fittig and Slocum (*Annalen*, **227**, 60), splits up when heated, yielding cinnamic and acetic acids,

$$\overset{O\cdot COCH_3}{C_6H_5\cdot CH}.CH\boxed{H}\cdot COOH = C_6H_5\cdot CH : CH\cdot COOH + HOCO\cdot CH_3,$$

the reaction taking place more easily in the presence of acetic anhydride.

The succinate of benzylidene does not appear to have yet been isolated, but there is no reason to doubt its existence. Its composition is the same as that of phenylparaconic acid, and its change into this compound may be thus written :—



Succinate of benzylidene. Phenylparaconic acid.

This acid on being heated also gives up carbonic anhydride, and phenylcrotonic acid is formed.

Why an acetate or other analogous salt should induce this intramolecular change in the benzylidene derivative is difficult to understand. It is possible that the two first form a compound, and the reaction may in some way be connected with the fact that the above salts containing feeble acids are capable of furnishing a base for the new acid. Thus in the formation of cinnamic acid I have shown that the product of the reaction contains a compound of sodium cinnamate and cinnamic acid.

Caro's method of formation of cinnamic acid, which is used technically, also bears upon this subject. It is well known that silver acetate and benzylidene dichloride yield benzylidene diacetate; if, however, sodium acetate is used, this acetate, although undoubtedly formed at first, yet changes directly it comes in contact with the sodium acetate, cinnamic acid being formed as the final result. I hope to make further experiments on the salts of benzylidene in reference to this subject.

These observations point to the condensation taking place between the aldehyde and anhydride, as do several of my older experiments. Thus I found that cinnamic acid could be formed whether the salt used were an acetate, butyrate, or valerate, but on these I would not

lay much stress, because it may be I was practically working to a large extent with an acetate, the acetic anhydride entering into double decomposition, butyric or valeric anhydrides and the salt being formed. And as the acetic anhydride was somewhat in excess, and the more active body at the temperatures employed, cinnamic acid would be produced, the other anhydrides taking no part in the reaction. But I also made an experiment which is the opposite of this, and has moreover been confirmed by the work of Conrad (*Annalen*, **204**, 188), and on this I do lay stress. I found that isophenylcrotonic acid could be formed from benzaldehyde and propionic anhydride apparently equally well whether sodium acetate or propionate were employed. But, as remarked by Tiemann and Kraaz (*Ber.*, **15**, 2061), anhydrides of acids richer in carbon would be feebler than those containing less carbon; therefore, acetic anhydride would turn out a compound richer in carbon from its sodium salt. It would be very improbable that the converse of this should take place to any considerable extent, and in fact, experiment goes to bear out this view.

I have, however, made some more experiments on this subject. It will be remembered that I found that when isobutyric anhydride was heated with benzaldehyde and an isobutyrate, instead of obtaining an unsaturated acid, carbonic anhydride and butenylbenzene were formed. It appeared to me, therefore, that this anhydride might be used in these experiments, because the carbonic anhydride given off might serve as a measure of the extent of the reaction. Fittig has shown that the first part of this reaction consists in the formation of phenylhydroxypivalic acid (phenylhydroxytrimethacetic acid) or its isobutyl-derivative, which are not very stable compounds, but when heated split up into carbonic anhydride and butenylbenzene. This, of course, does not militate against the following results, because the final products still show the amount of change which has taken place in the above direction. A mixture of benzaldehyde, isobutyric anhydride, and an acetate was therefore experimented with. Now if the salt be the agent with which the condensation takes place, cinnamic acid should be produced, and no carbonic anhydride; but if the anhydride, then carbonic anhydride and butenylbenzene should result. On heating this mixture, carbonic anhydride was evolved freely and in abundance, and butenylbenzene was also formed in quantity. In one experiment, the amount of carbonic anhydride obtained in relation to the aldehyde used was 24·2 per cent., and in a second experiment 22·5. The temperature of the oil-bath used was about 170°, and the time of digestion five and a half hours in one case, and six hours in the other. A small quantity of cinnamic acid was formed. A mixture of isobutyric anhydride, sodium isobutyrate, and benzaldehyde was then taken, to see what amount of carbonic anhydride this would

evolve in comparison with the preceding under similar conditions. The temperature of the oil-bath was 170°, and the heating was continued for six hours. The amount of carbonic anhydride formed amounted to 28 per cent. An operation was also made with isobutyric anhydride, sodium butyrate (normal) and benzaldehyde, a temperature of about 160° being used, and the digestion continued for five hours. This gave 21·6 per cent. carbonic anhydride, and only 17 per cent. phenylangelic acid.

In the above experiments, the proportions of the sodium salts and aldehyde used were molecular, the amount of anhydride being rather in excess of this proportion.

Three experiments were then made the reverse of the foregoing, that is to say, acetic anhydride and an isobutyrate were used with the benzaldehyde, molecular proportions being taken. These were not expected to give any very definite results, because double decomposition would be sure to take place between the anhydride and salt, so that it would be a queston as to the rate at which this would take place, compared with that of the combination of the anhydride and aldehyde. The results, however, show that cinnamic acid is produced in considerable quantity, and although carbonic anhydride and butenylbenzene are formed, their amount is comparatively small. The following are the results:—

	I.	II.	III.
Cinnamic acid	44·4	43·6	45·0
CO_2....................	10·1	11·0	7·4

The temperature at which the last experiment was made was about 160°, the others nearer 170°.

The largest yield of cinnamic acid I have obtained by heating acetic anhydride, an acetate, and benzaldehyde, was 84 per cent. on the benzaldehyde, so that these experiments have yielded over 50 per cent. of that obtained under the most favourable circumstances.

Fittig and Ott made experiments with a similar mixture, but used a temperature of 100° C., which had been previously shown by Fittig and Slocum (*Annalen*, **227**, 59) was too low to allow of cinnamic acid being formed under any circumstances. The formation of this acid, therefore, being prevented, phenylpivalic compounds, which are produced at this temperature, were gradually formed from the isobutyric anhydride which was slowly produced by double decomposition. This hypothesis is supported by the fact that when Fittig and Ott employed acetic anhydride, the formation of phenylpivalic derivatives took place very slowly, and only a small quantity was produced by heating at 100° for 20 hours, whilst when isobutyric anhydride was used the formation took place very much more quickly (*Annalen*, **227**, 79).

Other experiments are in progress in reference to this subject, but I now wish to refer to some results which have been obtained while studying the nature of this reaction, though they are not intimately connected with it.

While examining into the changes which take place when normal butyric anhydride, a butyrate, and benzaldehyde are heated together, a high temperature being used (the mixture being in fact boiled), it was noticed that carbonic anhydride was very slowly but continuously given off. At first it was thought that this might be due to the decomposition of the phenylangelic acid produced, but not being satisfied on this point, it was determined to make experiments with butyric anhydride and a butyrate, omitting the benzaldehyde, and on doing so it was found that carbonic anhydride was still evolved in a slow but regular manner, and when the volatile products were distilled, the distillate not only contained butyric anhydride, but also a neutral oil possessed of great stability.

Larger operations were then made. At first the proportions of anhydride to salt used were molecular, but afterwards an excess of anhydride was employed. The mixture was heated in a fractioning apparatus with a column about 2 feet long; this was connected with a condenser and a receiver, and this again with a potash bulb filled with sulphuric acid to observe the progress of the operations by the bubbles of gas passing. In one case bromine and water was used, to see if any absorbable gases were formed, but none were found to be produced. The mixture was kept boiling by means of an oil or fusible alloy bath, but only gently; a thermometer with its bulb in the mixture generally indicated a temperature of between 185° and 190°; this was maintained for about 36 hours, a small quantity of product being distilled over now and then. The temperature was then increased, so that nearly all the volatile products passed over. No appreciable increase in the formation of carbonic anhydride was observed during the extra heating, in fact it nearly ceased towards the end of the distillation.

The product when fractioned showed no definite boiling point, it was therefore treated with aqueous potash to remove butyric anhydride or acid, usually present in the anhydride. This, however, was not found sufficient, and as the oil did not appear to be decomposed by alcoholic potash, it was mixed with this in excess, and, after standing for some time, separated by the addition of water, and dried over potassium carbonate. On being fractioned, it commenced to boil at about 115°, the last parts not coming over until about 170° or 180°. After repeating this operation a few times, a boiling point was indicated between 140° and 150°, and eventually the principal part of the oil was obtained, boiling between 144·3° and 146·3°.

This gave on analysis the following numbers :—

I. Boiling point, 144·3—146·3°.
0·1433 gram substance gave 0·3885 gram CO_2 and 0·1592 gram OH_2.

II. Boiling point, 144—145°.
0·1458 gram substance gave 0·3937 gram CO_2 and 0·1617 gram OH_2.

	I.	II.	Calculated for $C_7H_{14}O$.
C	73·92	73·51	73·68
H	12·34	12·31	12·28

This substance is in fact butyrone, or dipropyl ketone.

The density determinations are pretty close to those given by Chancel. He gives 0·8195 at 20°. The above gave—

$$d\frac{4^\circ}{4} = 0·83048$$

$$d\frac{15^\circ}{15} = 0·82165$$

$$d\frac{25^\circ}{25} = 0·81452$$

Having only a limited quantity at my disposal, I do not assume it was quite pure, especially as these substances, having a very low specific heat, are very difficult to purify by fractioning, therefore the density must not be taken as absolutely correct for pure butyrone. This ketone is a very stable compound, and dissolves in concentrated sulphuric acid with heat, apparently combining with it, but on the addition of water it separates unchanged.

Isobutyric anhydride and sodium isobutyrate react in a similar manner, producing a neutral oil consisting of various ketones, but their examination has not yet been completed.

Having obtained the above results, similar experiments were made with propionic anhydride and a propionate. On boiling these products together, carbonic anhydride is given off, but very slowly indeed, the boiling point of the mixture being scarcely sufficient for the reaction. The mixture was therefore heated in sealed tubes at 180—190°. The amount of carbonic anhydride evolved was then sufficient to burst some of the tubes, in fact it was found best to open them after heating for three or four hours, and then to reseal and re-heat them. After the tubes were opened and the carbonic anhydride allowed to escape, condensing tubes were fitted to them, and they were heated in an air-bath up to about 200°, until no more fluid came over. This distillate was heated with aqueous potash, dried, and dis-

tilled; most of it came over between 99° and 109°, leaving some higher product; this was chiefly propionic anhydride, which had escaped the action of the aqueous potash. On refractioning the product, it again commenced to boil at 99°, but soon rose to 102°, when most of it came over between this and 103°. This substance gave on analysis the following numbers:—

0·1472 gram substance gave 0·3770 gram CO_2 and 0·1564 gram OH_2.

	Found.	Calculated for $C_5H_{10}O$.
C	69·84	69·76
H	11·80	11·62

This product was therefore *propione*. This ketone dissolves in concentrated sulphuric acid, and separates unchanged on the addition of water.

On preparing a quantity of propionic anhydride from sodium propionate and propionic chloride, and fractioning the product, a small quantity of oil of low boiling point was obtained. When purified, this boiled at the same temperature as propione, and had all its properties. This would be most probably produced by the action of the anhydride, as it was formed on some of the propionate which had escaped the action of the chloride, though it is just possible it might have been formed by the action of heat on some of the unchanged propionate during the process of distillation; the latter, however, is the less probable of the two.

Acetic anhydride was next heated with sodium acetate. No carbonic anhydride was given off, and on heating strongly acetic anhydride distilled over, leaving acetate of sodium behind. If, however, the mixture is heated in a sealed tube at 190—200° for three or four hours, carbonic anhydride is formed in quantity, and the product becomes brownish in colour. On opening the tubes and distilling off the volatile products, a colourless liquid was obtained, evidently containing acetic anhydride. On fractioning, a good deal passed over between 60° and 120°, and this on being refractioned gave a product boiling chiefly between 56·5° and 59·5°, which was evidently acetone, as it combined with sodium bisulphite, forming the ordinary easily soluble crystalline compound. It was not thought necessary to analyse it.

This reaction therefore appears to be general between the salts and anhydrides of the fatty acids. How can it be explained? Of course it is easy to understand that an anhydride, on losing carbonic anhydride, can yield a ketone, thus:—

$$\begin{matrix}R\cdot CO\\R\cdot CO\end{matrix}\!\!>O = \begin{matrix}R\\R\end{matrix}\!\!>CO + CO_2,$$

but an anhydride at the temperatures which have been used certainly does not undergo this change.

Again, a salt of a fatty acid when heated yields, as is well known, a carbonate and a ketone, but this decomposition requires a much higher temperature than was used in the foregoing experiments, in fact it was found that as soon as the mixture of the anhydride and salt had been heated sufficiently high to distil off all volatile products, no more carbonic anhydride or ketone was formed, so that this reaction does not explain the matter.

In a paper published in this Journal a good many years since (1868, p. 185), I showed that sodium acetate combined with acetic anhydride to form the compound $NaC_2H_3O_2,C_4H_6O_3$, already referred to, and there is no doubt that similar compounds are formed with other anhydrides and salts: in fact, when they are heated together the salts swell up, and a good deal of the anhydride disappears, and it seems to me that the production of the ketones is due to the formation and subsequent decomposition of such products, which are doubtless true chemical compounds.

It is well known that benzaldehyde combines with acetic anhydride to form benzylidene diacetate, which has already been referred to:—

$$\begin{matrix} H \\ C_6H_5 \end{matrix}\!>CO + O<\!\begin{matrix} CO\cdot CH_3 \\ CO\cdot CH_3 \end{matrix} = C_6H_5\cdot CH<\!\begin{matrix} O\cdot CO\cdot CH_3 \\ O\cdot CO\cdot CH_3 \end{matrix}.$$

Acetaldehyde also combines with acetic anhydride to form ethylidene diacetate.

If we apply this reaction to sodium acetate, which is simply aldehyde with an atom of hydrogen replaced by NaO, we get the following result:—

$$\begin{matrix} NaO \\ CH_3 \end{matrix}\!>CO + O<\!\begin{matrix} CO\cdot CH_2 \\ CO\cdot CH_3 \end{matrix} = \begin{matrix} NaO \\ CH_3 \end{matrix}\!>C<\!\begin{matrix} O\cdot CO\cdot CH_3 \\ O\cdot CO\cdot CH_3 \end{matrix}.$$

That this is the constitution of the compound $NaC_2H_3O\cdot C_4H_6O_3$, there is no reason to doubt, any more than in the case of the compound obtained from oil of bitter almonds and acetic anhydride. Now if this be the case, it is not difficult to see how this compound should yield a ketone and carbonic anhydride—

$$\begin{array}{l} NaO \\ \;| \\ C<\!\begin{matrix} O\cdot CO\cdot CH_3 \\ O\cdot CO\cdot CH_3 \end{matrix} = CO_2 + CO(CH_3)_2 + NaO\cdot CO\cdot CH_3, \\ \;| \\ CH_3 \end{array}$$

because it appears quite probable that the weakest part of the compound would be between the oxygen-atoms associated with the one carbon-atom and the acetyl-groups.

The production of butyrone may be represented in an analogous manner:—

$$\begin{array}{l}NaO\\C_3H_7\end{array}\!\!>CO + O\!<\!\begin{array}{l}CO\cdot C_3H_7\\CO\cdot C_3H_7\end{array} = \begin{array}{l}NaO\\C_3H_7\end{array}\!\!>C\!<\!\begin{array}{l}O\cdot CO\cdot C_3H_7\\O\cdot CO\cdot C_3H_7\end{array},$$

the latter compound breaking up as follows:—

$$\begin{array}{l}NaO\\ \quad|\\ \;C\!<\!\begin{array}{l}O\;CO\cdot C_3H_7\\O\;CO\cdot C_3H_7\end{array}\\ \quad|\\ C_3H_7\end{array} = CO_2 + CO(C_3H_7)_2 + NaO\cdot CO\cdot C_3H_7.$$

If this explanation be true, and the sodium salt actually takes a definite part in the reaction, it is clear, if a salt were used containing an acid differing from that from which the anhydride was produced, that unsymmetrical ketones should be formed, because the hydrocarbon radical of the acid should go to form part of the ketone. This was put to the test, and sodium acetate was used in conjunction with butyric anhydride, because if it entered into the reaction it would produce a ketone containing methyl, which could be easily separated from other kinds of ketones by acid sodium sulphite; sodium butyrate would also be formed.

The reaction in this case should be—

$$\begin{array}{l}NaO\\CH_3\end{array}\!\!>CO + O\!<\!\begin{array}{l}CO\cdot C_3H_7\\CO\cdot C_3H_7\end{array} = \begin{array}{l}NaO\\CH_3\end{array}\!\!>C\!<\!\begin{array}{l}O\cdot CO\cdot C_3H_7\\O\cdot CO\cdot C_3H_7\end{array}.$$

and then—

$$\begin{array}{l}NaO\\ \quad|\\ \;C\!<\!\begin{array}{l}O\cdot CO\cdot C_3H_7\\O\cdot CO\cdot C_3H_7\end{array}\\ \quad|\\ CH_3\end{array} = CO_2 + CH_3\cdot CO\cdot C_3H_7 + NaO\cdot CO\cdot C_3H_7.$$

On heating this mixture of sodium acetate and butyric anhydride, the reaction went on much in the same way as when sodium butyrate was employed, carbonic anhydride being regularly given off, but the combination of the salt and anhydride took place, apparently, more rapidly, so that it was necessary to add an excess of the latter to keep sufficient fluid present to allow the boiling to take place properly. The crystalline salt gradually changed in appearance, and after about 24 hours the product became perfectly fluid. The volatile products were then distilled off, leaving a mass of fused sodium salt, which was found to consist chiefly of sodium butyrate. By fractioning, the oily distillate was separated into three portions—

I	B. p. =	98—140°
II	,,	140—165
III	,,	165° and above.

The two first were mixed with sodium bisulphite and allowed to stand a few days. The first fraction gave a considerable quantity of a crystalline compound, the second gave no crystals, but a small quantity of it dissolved. The crystals and solution of bisulphite were separated from the undissolved oil, rendered alkaline, and then distilled until oil ceased to come over. This oil was collected, dried over potassium carbonate, and fractioned; it commenced to boil at about 87°, but soon reached 100°, and nearly all had come over when the temperature had reached 108°; when refractioned, it commenced to boil at about 80°, but soon reached 103°; the fraction boiling between this and 104·5° was selected for analysis. Although the yield of this product was considerable for the size of the operation, yet I did not have enough to fraction the product very thoroughly, and it is probable, judging from the boiling point of the product, that a little acetone was formed in the operation, and that a minute quantity of this was still contained in the product, as the numbers are a little low.

0·1467 gram substance gave 0·3718 CO_2 and 0·1531 OH_2.

	Found.	Calculated for $C_5H_{10}O$.
Carbon........	69·12	69·76
Hydrogen	11·59	11·62

Not having sufficient to refraction, it was combined with sodium bisulphite, with which it soon formed a crystalline compound. On analysis, this product gave the following result:—

0·2958 gram substance gave 0·1066 Na_2SO_4 = 11·68 per cent. Na.

The formula $C_5H_{10}O{\cdot}NaHSO_3,\frac{1}{2}OH_2$, which is the formula given for the compound of methyl propyl ketone, requires 11·56 per cent. Na, therefore there can be no doubt that this product was methyl propyl ketone; it could not be its isomeride diethyl ketone, as this only combines with bisulphite with great difficulty.

The oil unacted upon by the acid sulphite consisted chiefly of butyrone; that this substance should be formed is a necessary consequence of the reaction, because as the sodium acetate becomes converted into butyrate, this reacts with the butyric anhydride, and yields butyrone.

These results, therefore, appear to establish the view of the reaction which is given above.

There is one matter worthy of notice in connection with the formation of ketones by this new reaction, that is the formation of com-

pounds of lower and higher boiling point than the ketone which alone should be produced, and this seems to become more marked as the molecular weight of the compounds used increases. These products, which consist of ketones, I have not as yet been able to separate in a satisfactory condition for analysis, but hope to be able to do so.

The formation of higher and lower ketones also occurs when the calcium or barium salts of the fatty acids are distilled; thus the product obtained from calcium butyrate is said to distil between 100° and 160°; in the case of barium propionate the variation in tempera- is less, viz., 80—108°.

It was thought that by heating a mixture of an anhydride of a fatty acid with a formate, an aldehyde might be formed; it was found, however, that formates decompose very readily under these circumstances, giving off carbonic oxide.

Experiments are in progress with reference to the action of the anhydrides of bibasic acids on salts, but at present the results have been unpromising: thus, when succinic anhydride is heated with an acetate at about 190°, a black product is formed, which dissolves in part in boiling water with a brown caramel colour, leaving a brownish-black insoluble product.

ANNUAL GENERAL MEETING,

March 30th, 1886.

Dr. Hugo Müller, F.R.S., President, in the Chair.

On behalf of the Council I have the honour of submitting to you a report on the present state of the Society, and a brief account of its activity during the past session.

It affords me great pleasure to say that those indications of prosperity which were dwelt upon by my predecessors in the more recent Anniversary Addresses have not diminished, and that the increase in the numerical strength of the Society is still fully maintained. This will be borne out by the following statistics, quite apart from the financial details, which I leave to be dealt with by your Treasurer.

Number of Fellows, Anniversary, March, 1885......		1360
Since elected and paid admission fees..............		111
		1471
Deceased..................................	16	
Withdrawn.................................	8	
Removed on account of arrears...............	19	
		43
Present number of Fellows..................		1428
Increase 71.		
Honorary Foreign Members at last Anniversary	32	
Deceased..................................	1	
Present number............................	31	31
Total number of Members..................		1459

Thus, whilst the number of our members has increased to 1459, the loss we have sustained by death during the year is somewhat smaller than in the previous year. Amongst those, however, whom we have to regret are some of our oldest and most prominent members. The names of the deceased are; the honorary foreign member, Prof. Hermann von Fehling, Frederick Allen, Prof. Andrews, E. O. Brown, G. W. H. Clements, Frederick Field, F.R.S., James Higgin, Rev. S. Morris, James Parette, Thomas Spencer, Dr. E. G. Schweitzer,

Surgeon-Major Sheppard, Henry Shepheard, Alfred Tribe, Dr. John Smith, W. S. Ward, and Walter Weldon, F.R.S.

The obituary notices will be given hereafter.

Passing on to the consideration of what must always be looked upon as the principal function of our Society, it is particularly gratifying to notice the very marked increase in the number of the communications and papers during the past year.

The following are the titles of the papers in the order in which they were received:—

Papers contributed to the Chemical Society between March 30th, 1885, *and March 30th,* 1886.

April 2nd.

I. "On the Formation of Hyponitrites from Nitric Oxide:" by E. Divers and T. Haga.

II. "On the Existence of Barium and Lead Nitrosulphates:" by E. Divers and T. Haga.

III. "Notes on Fractional Distillation in a Current of Steam:" by M. E. Lazarus.

IV. "Derivatives of Taurine." Part I: by J. W. James.

V. "On the Preparation of Ethylene Chlorothiocyanate and β-Chlorethanesulphonic Acid:" by J. W. James.

VI. "The Orthovanadates of Sodium and their Analogues:" by Harry Baker.

April 16th.

VII. "A Crystalline Tricupric Sulphate:" by W. H. Shenstone.

VIII. "A Modified Bunsen Burner:" by W. H. Shenstone.

IX. "The Chlorination of Phloroglucol:" by C. S. S. Webster.

X. "Note on the History of Thionyl Chloride:" by C. Schorlemmer, F.R.S.

XI. "On the Reactions of Selenious Acid with Hydrogen Sulphide, and of Sulphurous Acid with Hydrogen Selenide:" by E. Divers and T. Shimidzu.

XII. "On a New and Simple Method of Quantitative Separation of Tellurium and Selenium:" by E. Divers and M. Shimosé.

May 7th.

XIII. "On some Points in the Composition of Soils; with Results illustrating the Sources of Fertility of Manitoba

Prairie Soils:" by Sir J. B. Lawes, Bart, LL.D., F.R.S., F.C.S., and J. H. Gilbert, LL.D., Ph.D., F.R.S., V.P.C.S.

XIV. "Researches on the Relation between the Molecular Structure of Carbon Compounds and their Absorption Spectra:" by W. N. Hartley, F.R.S.

XV. "Researches on the Action of the Copper-zinc Couple on Organic Bodies. Part X. Benzyl Bromide:" by J. H. Gladstone, F.R.S., and Alfred Tribe.

XVI. "On the Selective Alteration of the Constituents of Cast Iron:" by Thomas Turner, Assoc. R.S.M.

XVII. On the Existence of Nitrous Anhydride in the Gaseous State:" by G. Lunge.

XVIII. "On the Reaction between Nitric Oxide and Oxygen under Varying Conditions:" by G. Lunge.

May 21st.

XIX. "A Colorimetric Method for Determining Small Quantities of Iron:" by Andrew Thompson, M.A., B.Sc.

XX. "On some Sulphur Compounds of Calcium:" by V. H. Veley.

XXI. "Spectroscopic Observations on Dissolved Cobaltous Chloride:" by W. J. Russell, F.R.S.

XXII. "On the Sulphides of Titanium:" by T. E. Thorpe, F.R.S.

XXIII. "Note on the Formation of Titanous Chloride:" by T. E. Thorpe, F.R.S.

June 4th.

XXIV. "On the Constitution of the Haloïd Derivatives of Naphthalene:" by R. Meldola.

June 18th.

XXV. "The Decomposition and Genesis of Hydrocarbons at High Temperatures. I. The Products of the Manufacture of Gas from Petroleum:" by Henry E. Armstrong and A. K. Miller.

XXVI. "On the Non-crystalline Products of the Action of Diastase upon Starch:" by Horace T. Brown and G. H. Morris, Ph.D.

XXVII. "Decomposition of Carbonic Acid Gas by the Electric Spark:" by H. B. Dixon, M.A., and H. F. Lowe, B.A.

XXVIII. "On the Influence of Silicon on the Properties of Cast Iron:" by Thomas Turner.

XXIX. "Eleven Months' Experience with Toughened Glass Beakers:" by R. J. Friswell.

XXX. "Bromo-derivatives of Diphenyl, Tolylphenyl and Ditolyl: by T. Carnelley and Andrew Thomson.

XXXI. "Note on the Influence of Strain on Chemical Action:" by T. Carnelley and James Schlerschmann.

XXXII. "On the Non-existence of Gaseous Nitrous Anhydride:" by William Ramsay, Ph.D.

XXXIII. "On the Causes of the Decrepitation in Samples of so-called Explosive Pyrites:" by B. Blount.

XXXIV. "On the Specific Action of a Mixture of Sulphuric and Nitric Acids upon Zinc in the Production of Hydroxyamine:" by E. Divers and T. Shimidzu.

XXXV. "On the Action of Pyrosulphuric Acid on certain Metals:" by E. Divers and T. Shimidzu.

XXXVI. "On the Constitution and Reactions of Liquid Nitric Peroxide:" by E. Divers and T. Shimidzu.

XXXVII. "On the Behaviour of Stannous Chloride towards Nitric Oxide and towards Nitric Acid:" by E. Divers and T. Haga.

XXXVIII. "Preliminary Note on the Reactions between Mercurous Nitrate and Nitric Oxide, and between Mercurous Nitrate and Nitrite:" by E. Divers and T. Haga.

XXXIX. "On some Derivatives of Anthraquinone:" by A. G. Perkin and W. H. Perkin, Jun., Ph.D.

Papers Contributed to the Society during the Months of July, August, September and October.

XL. "On the Unit adopted for the Atomic Weights:" by Lothar Meyer and Karl Seubert.

XLI. "The Atomic Weight of Silver, and Prout's Hypothesis:" by Lothar Meyer and Karl Seubert.

XLII. "A Method for Obtaining Constant Temperatures:" by W. Ramsay, Ph.D., and Dr. Sydney Young, D.Sc.

XLIII. "Researches on Secondary and Tertiary Azo-compounds." No. III: by R. Meldola.

XLIV. "Note on the Spontaneous Polymerisation of Volatile Hydrocarbons at the Ordinary Atmospheric Temperature:" by Sir Henry E. Roscoe, F.R.S.

XLV. "On the Action of Gypsum in Promoting Nitrification:" by R. Warington.

XLVI. "Contributions towards the History of Formyl and Thioformyl Compounds derived from Aniline and Homologous Bases:" by Alfred Senier, M.D.

XLVII. "Action of Phenyl Cyanate on Polyhydric and certain Monohydric Alcohols and Phenols:" by H. Lloyd Snape, B.Sc.

XLVIII. "Chemical Examination of the Constituents of Camphor Oil:" by Hikorokuro Yoshida.

XLIX. "On the Synthetical Formation of Closed Carbon Chains:" by W. H. Perkin, Jun., Ph.D.

L. "Action of Sodic Alcoholates on Ethereal Fumarates and Maleates:" by T. Purdie, Ph.D., B.Sc.

LI. "Contributions to the Chemistry of the Cerite Metals." III: by B. Brauner, Ph.D.

LII. "A New Method of Preparing Aromatic Hydrocarbons:" by Richard Anschütz.

LIII. "On the Decomposition of Aromatic Ethereal Salts of Fumaric Acid:" by Richard Anschütz and Quirin Wirtz.

LIV. "On an apparently New Hydrocarbon from Distilled Japanese Petroleum:" by E. Divers and T. Nakamura.

November 5th.

LV. "The Influence of Silicon on the Properties of Cast Iron." Part II: by Thomas Turner, Assoc. R.S.M.

LVI. "Modifications of Double Sulphates:" by Spencer Umfreville Pickering, M.A.

LVII. "The Relation of Diazobenzene-anilide to Amidoazobenzene:" by R. J. Friswell and A. G. Green.

LVIII. "An Examination of the Phenol Constituents of Blast Furnace Tar obtained by the Alexander and McCosh Process at the Gartsherrie Iron Works:" by Watson Smith, J. F. H. Coutts and H. E. Brothers. Part I.

LIX. "The Decomposition of Potassium Chlorate by Heat:" by Frank L. Teed, D.Sc., F.C.S.

LX. "Note on the Refractive Power of Metacinnamene (Metastyrole):" by H. G. Madan, M.A., F.C.S.

November 19th.

LXI. "Aluminium Alcohols. Part III. Aluminium Orthocresylate and its Products of Decomposition by Heat:" by J. H. Gladstone, F.R.S., and Alfred Tribe.

LXII. "Notes on the Constitution of Hydrated and Double Salts:" by Spencer U. Pickering.

LXIII. "Some New Vanadium Compounds:" by J. T. Brierley.

LXIV. "On the Action of Phosphorous Pentachloride upon Ethylic Diethylacetoacetate: by J. W. James.

XCIX. "The Identity of certain Mixed Ethereal Oxalates:" by L. Gordon Paul.

March 18th.

C. "The Combustion of Cyanogen:" by Harold B. Dixon, M.A.

CI. "Note on the Constitution of the Naphthalene-derivatives:" by R. Meldola.

CII. "Action of Ammonia on Chromyl Dichloride:" by S. Rideal, B.Sc.

CIII. "Note on the Estimation of Resin in Soaps:" by C. R. Alder Wright, D.Sc., F.R.S.

CIV. "The Properties of the Nitrobenzalmalonic Acids:" by Charles M. Stuart, M.A.

It will thus be seen that the number of papers communicated has reached 104, which is not only a very great advance on the previous year, when the number was only 67, but with the exception of the session of 1880–81, when it was 113, it is the largest number hitherto attained. These contributions embrace a wide range of subjects, and most of the branches of our science are represented amongst them. A glance at the list calls to mind the great interest and appreciation with which many of them were received and discussed at the meetings. This increase in the number and importance of the communications has rendered it necessary, in order properly to get through the business at these meetings, to adhere more strictly to the practice of giving abstracts only of the papers presented.

But not only is this revival of chemical research evidenced by the number of papers, but also by the greatly augmented size of the volume in which they are recorded; this is nearly one-third larger than that of the previous year, and almost twice as large as that of 1883–84.

The future will show whether this satisfactory result is merely accidental, or whether it really indicates the wished-for awakening of activity in the direction of chemical research.

I am inclined to think that it is due in no inconsiderable degree to the fact that the various new laboratories which have been established in the country during the last few years are now gradually entering upon their full activity. With the extending opportunities which will be afforded to the younger generation of chemists by these laboratories, we may look forward with confidence to a continuous and steadily increasing development in the pursuance of scientific chemical work in this country.

In the course of the year we have had one lecture—delivered by Prof. Klein—on "Methods of Bacteriological Research from a Biologist's Point of View," which proved both highly interesting and instructive. The chemical study of the life processes of these low organisms has already afforded most valuable results, and, in conjunction with further and closer examination of the phenomena connected with the action of the ferments generally, will open out a vast field for chemical investigation of both scientific and practical importance.

As the identification of the particular organisms which are concerned in these complex processes becomes more and more of importance, a thorough acquaintance with the methods of pure cultivation of these organisms must be considered as of special value, and Dr. Klein has rendered a much appreciated service to the Chemical Society by giving us the benefit of his great experience, gained in his own work in this direction.

The experiment of publishing in a separate form the "Abstracts of the Proceedings of the Society" has now been continued for more than a twelvemonth, and I think you will agree with me that the result has realised the object which prompted your Council in deciding upon its initiation. The utility of this publication is particularly appreciated by our country members, who are thus kept in touch with the doings of the Society. The Honorary Secretaries still continue to charge themselves with the editorship, and our best thanks are due to them for the zeal and promptitude with which they discharge this self-imposed duty.

The Publication Committee is fully alive to the desirability of effecting the publication of the Journal with the least possible delay, and in this respect some notable progress has been made, thanks to the efforts of our Editors.

I have also to direct your attention to that part of our publication which contains the Abstracts of Papers published in other Journals. The enormous amount of matter which has to be abstracted and incorporated into this volume had at the end of last year got somewhat in arrear, but thanks to the vigilance of the editors this difficulty has been overcome, and the Abstracts are now up to date.

In connection with this, I have to acquaint you with a recent resolution of your Council as to the Abstracts of Papers on Technical Chemistry. Whilst it has been felt all along that these Abstracts, on account of their brevity, only very imperfectly fulfilled their object, a more liberal treatment and greater completeness were considered to be incompatible with the means at our disposal. After mature consideration, the Council decided upon the discontinuance of these Abstracts in the manner in which they have hitherto appeared, and for the future only such papers on Technical Chemistry are to be abstracted

and published as involve a new process, or possess otherwise a special scientific interest. Previous to the foundation of the Society of Chemical Industry, it was a matter of importance that Abstracts of Technical Chemical Papers should, however short, find a place in our Journal, but since the above-named Society has made it a special object to publish in their excellent Journal comprehensive and full abstracts of all technical chemical papers, as well as of patents, it was thought that for the future we could not do better than leave this matter in such competent hands.

Ever since the Chemical Society took possession of its present home the extension and improvement of the library have been one of its principal aims, and the Committee appointed for this object have done their utmost to apply the means placed at their disposal to the best advantage. Thus from year to year considerable and important additions have been made, which are rapidly filling up the empty spaces formerly so conspicuous in the bookshelves.

You will have noticed that a very considerable addition of space for books has lately been gained by the new bookcases fitted up in the tea room, and I may remark that these have been put up at the expense of the Society, whilst the others in the library were taken over with the premises as fixtures, and belong therefore to the Government.

In the last Anniversary Address, it was mentioned that the catalogue of the library which was then in progress was nearly completed, and I have now the pleasure of announcing to you that this laborious task has just been finished, thanks to the assiduous energy of Messrs. McLeod and R. Warington, and of your librarian, Dr. Thorné. In the course of this work, it became evident that it was absolutely necessary to check the presence of each volume enumerated in the previous catalogue, and this, quite apart from the actual preparation of the catalogue itself, involved a vast amount of labour, which has been the main cause of the long delay.

The catalogue is now ready, and is being distributed to the members. Your Council trust that its improved arrangement will meet with the approval of the Fellows who are in the habit of using the library.

This may be deemed a fitting occasion for bringing under your notice a statement drawn up by Dr. Thorne, which shows the additions to the Library made under the various headings, as far as the present rearrangement and classification of the books permit a comparison with the account given three years ago.*

* In this statement the apparent decrease in "Technical Chemistry" is due to the removal of pharmaceutical and medical works to a separate section, and of some few other works to other sections. Works on meteorology are now included under "Physics;" and dictionaries are placed under the various sections to which they belong. The decrease in the number of *volumes* of systematic works from 2600 to 2420

	1883.	1886.	
Physics	255	288	
General Chemistry	256	326	
Inorganic Chemistry	49	68	
Organic Chemistry	58	76	
Physiological Chemistry	87	121	
Vegetable Physiology and Agriculture	110	146	
Analytical Chemistry	165	217	
Technical Chemistry	356	270	
Mineralogy and Geology	103	121	
Meteorology	16	—	
Biography	8	15	
Miscellaneous	33	84	
Dictionaries	23	—	
Pharmaceutical and Medical	—	71	
	1519	1803	(increase 284)
Volumes of systematic works	2600	2420	
Volumes of Journals, &c.	3600	4750	
Volumes of Duplicate Journals, &c., for circulation	600	830	
	6800	8000	(increase 1200)
Pamphlets	760	1380	(increase 620)

Satisfactory as the steady growth of the library undoubtedly is, there is, however, a difficulty looming in the distance; for as we may hope that this development will continue, the space at our disposal will become less and less, and very shortly the question of providing fresh accommodation will arise.

As an event which has taken place during the past year, and which is of special interest to this Society, I must not omit to mention the Incorporation by Royal Charter of the Institute of Chemistry.

It will be within the recollection of some of those present that about ten years ago a very strong desire was manifested by some of our members that this Society should assume an authoritative position for regulating and advancing the professional status of chemists,

is probably due to many of the old and short sets of periodicals having in 1883 been counted amongst the volumes of systematic works. This would to some extent account for the abnormally large increase (1750) in "Volumes of Journals, &c.," although this is due in part to the completion of imperfect sets.

with the view of ultimately obtaining the official recognition of chemistry as a profession. This movement caused at the time a good deal of perturbation, and seriously engaged the attention of those who took a hearty interest in the welfare of this Society; but after earnest consideration of the various means proposed for carrying out the object desired, it was found that the Chemical Society was debarred by the articles of its Charter from giving effect to it.

Subsequently, an association was established with the special object of bringing about a definite organisation of professional chemists, and after having during the last eight years gradually developed its aims and matured its plans, it has acquired an official acknowledgment of its public utility by receiving a Royal Charter of Incorporation.

The Institute of Chemistry has thus entered upon a new career which bids fair to confer a great benefit on all who are engaged in the pursuit of chemistry in this country.

Regarding then from our Society's point of view, the Institute of Chemistry, in its present constitution, with its public duties and its public responsibilities, I think we must rejoice that the originators were forced by circumstances at an early stage of its initiation to attempt the realisation of their laudable efforts on an independent basis. It is quite inconceivable that the Chemical Society could have taken charge of these new functions in their entirety without seriously hampering the pursuits of its original and special object. But whilst this issue in itself is a matter of congratulation, there is still another aspect not less noteworthy, for we may anticipate that the incorporation and official establishment of the Institute of Chemistry will exert a direct and powerful influence on the development of chemical education, which in its turn must assuredly promote the progress of pure chemical science.

With regard to the operation of the Research Fund, I may state that during the past year nine applications have been granted by the Research Fund Committee, and the sums thus expended amount altogether to £155, leaving even on the present somewhat reduced income of £268 (of which sum £180 to £190 is derived from the funded property) a very considerable balance, which in this instance is perhaps not altogether a subject for congratulation.

As it might be expected from the foregoing statements that the increased activity of the Society would have caused a proportionate rise in the ordinary working expenses consequent upon the cost of our enlarged publications, it is of importance to point out that we have kept well within the means afforded by our income. For reasons which will become apparent on a perusal of the financial statement, last year's expenses were actually somewhat less than in the previous year, and consequently the increment in the income

leaves us with a considerably larger balance, even if we make the deduction for the probable expense of printing the catalogue which has not yet been charged.

During the session ending March, 1884, the total expenses of the Society were £2706, and the income £3536, leaving a balance of £830; in the session ending March, 1885, the total expenditure was £3284, with an income of £3569, leaving a balance of £285. In the year now ending the total working expenses of the Society amount to £3108, whilst our income has been £3743; leaving thus a balance of £635.

In bringing this report to a close, I cannot refrain from expressing the gratification I feel in having the privilege of testifying to the manifest progress in the activity of our Society, and to the otherwise prosperous condition of its affairs.

This is all the more encouraging when we look back upon those years of its career when its activity seemed to languish, and the prospects of its development were not hopeful. But some of my predecessors who had occasion to refer to this state of things, and who lamented over the apparent stagnation in the cultivation of scientific chemistry in this country, when compared with what was being done elsewhere, have perhaps not sufficiently recognised some points which I think deserve to be more fully considered.

Thus it appears to me that sufficient cognizance was not taken of the adverse influence of the eminently active life which surrounds us here, and which lays everyone more or less under contribution for co-operation in the attainment of that pre-eminence which this country holds in commerce as well as in manufactures. And those who are engaged in the pursuit of chemistry cannot help being drawn into this all-absorbing vortex.

I will only refer to the vast amount of valuable work which is continually emanating from the large and important associations, the Iron and Steel Institute, the Society of Chemical Industry, and also in a minor degree, the Society of Public Analysts, each of which, in its special line, represents chemical activity in this country.

Those who formerly entered on the study of chemistry, mostly did so with a view to its ultimate practical application, and strove in perhaps undue haste to attain this object. Under such conditions individuals who had the qualification, the means, and the leisure to devote themselves to scientific chemistry were naturally but few.

Now if we enquire into the causes which favoured the development of scientific chemistry in so marked a degree in other countries, we find that it took its rise in the seats of the higher education, in the universities, where its study was carried on on a level with that of other sciences, whilst its immediate utilisation for practical purposes remained for a considerable period in abeyance, and, therefore, the

material advantages accruing from it to the public at large were but small. In the course of time, however, its general diffusion produced its effect on the development of the arts generally, and gave more especially a powerful impetus to the progress of technical chemistry in its various branches.

This latter fact being now fully recognized in this country, great efforts are being made to stimulate the cultivation of scientific chemistry, and the establishment of late years of numerous laboratories throughout the country, to which I have already referred, cannot fail, in due time, to contribute their share towards the general advancement of our science, a result which this Society in particular must hail with acclamation.

Mr. FREDERICK ALLEN was born at Dartford, Kent, in 1809. He was educated privately, and apprenticed to an eminent firm of manufacturing chemists in London.

In 1833 he commenced business operations, devoting his attention specially to the production of oxalic acid and the oxalates. Subsequently he took much interest in the manufacture of artificial manures, and at a later period, in the early days of the coal-tar industry, was among the first to produce nitrobenzole and aniline on a manufacturing scale.

He was a thorough practical chemist, very energetic, and always desirous of furthering the interests of chemical industry.

THOMAS ANDREWS was a native of Belfast, and was the son of a local merchant. It was in this town he received his early training, and here, too, in the old Belfast College, of which he afterwards became one of the professors, he obtained his more advanced education; he also spent some sessions in Edinburgh University and Trinity College, Dublin. Having completed his collegiate course, which was a most successful one, and obtained his degree of M.D., he settled down in Belfast as a medical practitioner. After the lapse of a comparatively short period, he was appointed to the Chair of Chemistry there, and it may be remarked, as showing the high reputation which he had acquired at that early stage of his professional career, that, at the time of his acceptance of the professorship, he had at his choice two lectureships—one in Dublin and the other in Edinburgh. Dr. Andrews, however, chose to remain in Belfast, continuing his practice as a medical man, and attending, at the same time, to his professorial duties. Thus he continued up to 1846, when, the founding of the Queen's University in Ireland having been decided

upon, he was selected as Professor of Chemistry and Vice-President in Belfast Queen's College—a dual office which he certainly adorned. At the same time the Rev. Dr. Shuldham Henry, of Armagh, was appointed President, and it was largely under the direction of these two gentlemen that the College buildings were reared. President Henry and Vice-President Andrews afterwards lived for many years in their adjacent residences in the College buildings, and both resigned their respective offices at the same period. It was not until 1849 that the new College was opened, and then Dr. Andrews having commenced in it his duties as Professor, began to devote himself greatly to original research, especially as regards the specific heats of different substances. He afterwards gave much time to researches in reference to ozone, and in later years applied his great powers to the condensation of gases. Two of his papers on the liquefaction of gases were chosen as the Bakerian Lectures of the Royal Society. The first of these was in 1876, and the second shortly afterwards, and he had the high honour of reading both before the members of the Society. Dr. Andrews never devoted much time to literary work, but, in addition to several scientific papers, he published in 1868 a pamphlet entitled "Studium Generale; or, a Chapter of Contemporary History," dealing with the question of Irish university education. In 1876, however, when the British Association visited Glasgow, Dr. Andrews was chosen to the distinguished position of its president, and on that occasion he delivered a remarkably able and exhaustive review of the advancement of science in general. In 1879, in consequence of increasing infirmities, he resigned his official connection with the Queen's College, and was succeeded in the chair of chemistry by the present occupant, Dr. Letts. He then went to reside at Fortwilliam Park, and there he passed away after a prolonged period of illness. Dr. Andrews was an honorary LL.D. of the Universities of Dublin, Glasgow, and Edinburgh, He was a Fellow of the Royal Society, Fellow of the Chemical Society of London, and Honorary Fellow of the Royal Society of Edinburgh. In the Queen's College, he was a great favourite with the students, who ever manifested a thorough appreciation of his masterly lectures. Long after the students had completed their training, he evinced the greatest interest in their welfare, and took special delight in watching their advancement and prosperity. It will be remembered that on Dr. Andrews' retirement from the College a life-size portrait of him was placed in the Common Hall, and he was presented with a replica for his own residence. In addition to adorning the College walls with his likeness, further honour was conferred upon the Doctor by the founding of the Andrews' Scholarship. Dr. Andrews was married to a Scotch lady, Miss

Walker, daughter of Major Walker, who survives him, and by whom he leaves three daughters and two sons, one of whom is a major in the army and the other a member of the Irish bar. It may be stated that Lord O'Hagan and Dr. Andrews were most intimate friends. They were schoolboys together, and the close friendship which was then formed continued unbroken. Only two years last autumn, when the late Lord O'Hagan himself was not at all well, he came to Belfast with the express object of paying a visit to Dr. Andrews. That was the last visit he paid to this town, to which he was so much attached. The death of this eminent scientist will be received with deep regret, not only in all parts of the United Kingdom, but throughout the scientific world.

Edwin Ormond Brown was born in the year 1828, at Devonport, where he served his time as an apprentice to a chemist and druggist. From an early age, he exhibited much interest in scientific pursuits, his leisure time being chiefly devoted to his favourite branches of study, Chemistry and Electricity.

His associates (amongst whom were several medical students) fully appreciated the talent he possessed of imparting to others in a clear and concise manner the knowledge he had acquired, and with the progress of time and increased experience this talent developed itself more fully, as will be allowed by all those who have benefited by his instruction.

In 1849 he entered as a student at the College of Chemistry under Dr. Hofmann. Here he gained the character of being an earnest investigator, eager to obtain a thorough knowledge of chemical science, and displaying great originality of ideas when the various theories propounded by eminent chemists came under discussion. After leaving the College, he became Lecture-Assistant to the late Dr. Stenhouse at Saint Bartholemew's Hospital, and subsequently assistant to Professor Way.

In 1856, he was appointed an assistant chemist of the War Department. Some of his earlier work consisted in an investigation of commercial coppers; during this he devised a more exact method of determining copper than had been previously known, which was published in the Society's Journal, 1858, and still continues to be used as one of the most exact and rapid methods of determining copper.

In 1862, the War Office determined that the question as to whether gun-cotton could be manufactured in such a form as to be capable of being used in the Service as an explosive agent should be thoroughly investigated by Professor, now Sir Frederick, Abel, and during the five years from 1863 to 1868, experiments were made on a somewhat considerable scale at Waltham Abbey, until a safe and efficient

process of manufacture had been established. These experiments were conducted by Mr. Brown, and the fact that they were carried out without a single accident of any importance speaks highly for the care and talent he displayed. He continued to be employed in investigations connected with the applications of gun-cotton, as well as other explosives, until his death.

Amongst the numerous valuable results obtained from his investigations, one of the most important was the fact that gun-cotton when converted into the pulped compressed condition as devised by Sir Frederick Abel was susceptible of being detonated whether in a dry or wet condition, by which the greatest amount of force it was capable of developing could be very readily utilised.

In 1876, Mr. Brown undertook the teaching of the Instructors in Gunnery of H.M. ship "Excellent," as well as voluntary classes of naval officers, in applied electricity, thus commencing a system of instruction which afterwards developed into the establishment of a Naval Torpedo School at Portsmouth. He also instructed classes of Royal Artillery officers and cadets in applied electricity and in the military applications of explosives.

Mr. Brown died very suddenly on the 5th December, 1885, after a few days' illness, no apprehension of his being in any danger having been entertained by his medical attendant until the morning of the day on which he expired.

George William Holliday Clements, F.C.S., was born at Carmarthen, South Wales, in 1857. When ten years old he was sent to a private grammar school, at St. Helen's, Lancashire, conducted by Mr. Thomas Bournes, under whose tuition he soon mastered the simpler elements of chemical science. When scarcely 15, he was apprenticed to Mr. J. A. Phillips, then Managing Director of the Widnes Metal and Smelting Works, at Widnes, Lancashire. Under the supervision of this celebrated chemist, he made rapid progress in mastering the technicalities of the science, both in the laboratory and by practical operations in the works. Here he continued for nearly five years, when a vacancy having taken place in the Laboratory Department of the Rio Tinto Copper Mines, at Huelva, in Spain, he was nominated to that post by Mr. Phillips, then Consulting Engineer to the Company. Mr. Clements went out to the mines in December, 1876, and for about two years (with entire satisfaction) filled the position of assistant chemist there.

He returned to England at the end of 1878, and for some time was engaged in analytical work in London, chiefly in the laboratory of Messrs. Mattheson and Co., the former proprietors of the Rio Tinto Mines. In the early part of 1880, he was offered the post of Analyst

(and Assayer of Ores) to the Bilbao Iron Ore Company Limited, in the north of Spain. For three years he held this responsible position, until the company ceased mining operations.

For the two last years of his life, he practised in Bilbao solely on his own account, as an analytical chemist and assayer of metallic ores. Owing to his sound practical experience in chemical analysis, knowledge of mines and minerals in general, with a character full of energy and enterprise, combined with high moral principles, he never failed to secure the confidence and support of his patrons, and all with whom he had intercourse. Had his life been spared there is hardly any doubt but that he would have made his mark in inventive science. In his spare moments, he projected many ingenious suggestions in mechanical science, improvements in locomotive engines, utilisation of tidal forces, &c., &c., which if spared, he hoped more fully to develop.

He died at the early age of 27, at Cumino de Santioce, Portugalate, Spain, on the 4th May, 1885, after a very brief illness, from congestion of the lungs, and was interred in the English cemetery, Bilbao, Spain. A monumental tablet was erected by express wish and at the sole cost of the English residents there, as a mark of respect to his memory. He has left a young widow and one posthumous child.

Hermann von Fehling was born on the 9th of June, 1812, at Lübeck. Originally intending to devote himself to pharmacy, he entered, about the year 1835, the University of Heidelberg, where he worked in Gmelin's laboratory. After graduating at Heidelberg, he removed to Giessen, where his earliest researches were carried out under Liebig's guidance. His first published work was a refutation of E. Davy's statement concerning the isolation of fulminic acid. During the Giessen period, he also investigated with success the polymerides of aldehyde and the composition of the salts of sulphobenzoic acid.

Soon after completing his studies, Fehling was appointed, on Liebig's recommendation, to be Professor of Chemistry in the Polytechnic at Stuttgart, a post which he held for more than forty years. At first his time was fully occupied in organising the chemical department of the institution, but as soon as his duties permitted he returned to the prosecution of his researches. His work on ammonia, on the palladium-ammonia compounds, and his monograph on succinic acid, date from this period. About this time, too, in 1844, Fehling carried out one of his most important investigations—that which led to the discovery of benzonitrile. This compound, which he obtained by the elimination of the elements of water from ammonium benzoate, was the prototype of the class of organic nitriles. It

is interesting to note that Fehling was fully alive to the bearings of this experiment; for not only does he, in stating his results, refer to the analogous transformation of ammonium formate into hydrocyanic acid discovered by Pelouze, but he calls attention to Döbereiner's almost forgotten experiment in which cyanogen is obtained from ammonium oxalate.

Later on, Fehling deserted pure chemistry for subjects of more practical interest. His professorship at the Polytechnic School, and the various other official appointments which he simultaneously held, directed his energies into these new channels. Questions of technology and of public health mainly occupied his attention. A list of the various subjects of this nature which he investigated could not be compressed within the limits of this notice. He also devised several new analytical methods, the best known of which is that for the determination of sugars by means of the solution which bears his name.

In spite of the constant pressure of professional and other official duties and of his experimental researches, he succeeded in accomplishing an amount of literary work which might have filled the entire time of a less energetic man. The German edition of Payen's *Chimie Industrielle* is from his pen. He took an active part in bringing out the later editions of Graham-Otto's *Text-book of Chemistry*. He was a contributor to the *Handwörterbuch* of Liebig, Poggendorff, and Wöhler, and when the *Neues Handwörterbuch* was to be produced, Fehling undertook the task of editing it, a work which he has not lived to complete. For many years he was a member of the Committee appointed for the revision of the *Pharmacopœia Germanica*.

He died on the 1st of July, 1885.

Frederick Field, F.R.S., F.C.S.E., Member of the Institute of Santiago de Chile, &c., was born in Lambeth, August 2nd, 1826. He was the second son by the second marriage of the late Charles Field, partner in the old established firm of J. C. and J. Field, wax bleachers and manufacturers of wax and sperm candles. He received his early education partly at Denmark Hill Grammar School, and partly by private tuition. He afterwards went to Mr. Long's School at Stockwell, in 1841, where he was a schoolfellow of Professor Odling. Young Field left Stockwell at the end of a year, and having from childhood evinced a great partiality for chemical science, he was placed in the Laboratory of the Polytechnic Institution, in 1843, at that time conducted by Dr. Ryan.

From the very popular nature of the Institution, Field's progress was not satisfactory, he however did his best to acquire some practical

knowledge of chemistry there, and was a diligent reader in his evenings at home of the works of Brande, Graham, Daniel, and others. The late Mr. Mitchell, a consulting chemist of some repute, soon afterwards induced Mr. Field to join him in his laboratory as an assayer and analytical chemist, another ill advised step which he took, as although he had spent much time in the assay of metals by the "dry" process in the laboratory of the Polytechnic, he was far too young and inexperienced to combat with the many difficulties with which he was surrounded, and to make himself responsible for the mercantile worth of valuable cargoes of mineral or other natural products. His own sense of his want of greater knowledge led him, as soon as the Royal College was established, to enlist himself as a pupil under Dr. Hofmann, who was at that time ably supported by the late Dr. Blythe. It was at this time that Mr. Field was elected a Fellow of the Chemical Society (1846), and he soon after published his first paper "On the Products of the Decomposition of Cuminate of Ammonia by Heat, and on Nitrobenzamide," which was read before the Society in 1847. There was a certain interest attached to this paper, as "Cümonitrile," one of the products of the decomposition of cuminate of ammonia, was the second of that interesting class of bodies yet discovered, Fehling having previously described benzonitrile.

In the autumn of 1847, Field was offered an appointment as chemist to a copper smelting establishment about to be erected in the province of Coquimbo, Chili, South America. Although very anxious to pursue his researches under the able guidance of Dr. Hofmann, domestic circumstances induced him to accept the offer, and he arrived in Chili at the commencement of 1848. There was, of course, considerable delay in erecting an establishment of the kind, but by dint of great perseverance on the part of the superintendent, Mr. Alison, the smelting of copper ores on a large scale commenced early in 1849. There is a paper by Field, in the *Journal of the Chemical Society*, 1850, "On the Examination of some Slags from Copper Smelting Furnaces." As the process of smelting used in Chili differed somewhat from that in England, the results of the examination proved not unworthy of note. There is also another paper on the ashes of the cactus, a plant which grows luxuriantly in these climates, and which was of interest from the large amount of carbonate of soda it yielded, derived from the sodium oxalate which exists abundantly in the plant. In 1851, Field published a description of a natural alloy of silver and copper, which bore a great resemblance to nearly pure silver, and proved sadly disappointing to the discoverers of the mine. An interesting circumstance occurred soon after this. A large quantity of ore arrived at the establishment, supposed to

be the blue carbonate of copper (chessylite), not an uncommon mineral in the neighbourhood of Coquimbo. Great was the indignation of the importer when he was informed by Mr. Field that his cargo did not contain a trace of the metal. It was, however, far too interesting to pass unnoticed, and on a minute examination it was found to be a pure lapis lazuli, the first found in South America, and Field was able to prove conclusively, that the sulphur did *not* exist as sulphuric acid, but as a sulphide, inasmuch as after digestion in strong acetic acid and evolution of sulphuretted hydrogen no trace of sulphur could be detected.

In 1852 it was proposed by the company in which Field was engaged, to establish smelting works in Caldera, a new port north of Coquimbo, on the confines of the desert of Atacama, in the neighbourhood of a district peculiarly prolific in copper and silver ores, and he was appointed manager of the new works. After an absence of five years he revisited England, in November, 1852, and soon afterwards married a sister of Sir Frederick Abel. He returned to Chili in the spring of 1853, and went at once to Caldera, which, although a new port, was rapidly increasing in importance. A railway was already established (the first on the western coast of South America) between the port and the city of Copiapo, and every inducement was afforded to foreigners, as well as the natives of the country, for the exploration of that district, the trade of which soon became of such importance that a British Consulate was deemed necessary, and Field had the good fortune to be appointed Vice-Consul in 1853. The duties of this post were not very arduous at certain seasons, but occasionally there was sufficient work to occupy many hours each day, especially during the period of the Russian War, when, owing to France not being represented, Field was desired by the late Admiral Harris, Chargé d'Affaires in Santiago, to assume the duties of French Consul in addition to those of England, and to afford the same protection to Frenchmen as he would to those of his own nation. In 1856, Field left the company in which he had been engaged for so long, and was appointed as chemist and under manager to a smelting establishment at Guayacan, which, though small in its beginning, is now perhaps the largest copper works in the world.

In 1859, a revolution of very formidable proportions broke out in Chili. The revolutionary party, headed by Don Pedro Gallo, marched from Copiapo, and after some days' journey arrived at Coquimbo, where a battle was fought between them and the Government troops, the latter being completely routed. As the establishment in which Field was now manager belonged almost exclusively to Señor Urmeneta, a zealous partisan of the Government, his position was very difficult and somewhat perilous; moreover, he had just been

appointed Acting Consul by the Chargé d'Affaires, in the absence of the Consul. Mr. Field, however, managed to send his wife and family to England, and remained at his post until the revolution had subsided, when he had the gratification of restoring the establishment, almost intact, into the hands of its owner, after which he left Chili, and arrived in England in September, 1859. He was appointed Lecturer of Chemistry at St. Mary's Hospital, in 1860, and Professor of Chemistry at the London Institution in 1862. In the autumn of that year, his old friend and fellow student, Mr. E. C. Nicholson, then of the firm of Simpson, Maule, and Nicholson, offered him a situation as chemist to their Aniline Colour Works, where he remained until 1866, when he became a partner in the house of J. C. and J. Field. The numerous duties incidental to so large a business precluded him, during the last few years of his life, from devoting his energies to the pursuit of his favourite science. His health, moreover, began to fail him very much in 1876, and he had to pass two winters entirely away from England. For the last two years of his life, he was a great and patient sufferer, and he died on Good Friday, April 3rd, 1885, at the age of 58.

The following may be quoted as among the more important of Mr. Field's contributions to chemical science:—"On the Products of the Decomposition of Cuminate of Ammonia by Heat and on Nitrobenzamide;" "On the Composition of the Ashes of the Cactus," "Description of Lapus Lazuli, found in Large Quantities in the Cordilleras of the Andes;" "On the Composition of a Specimen of Atacamite from the Province of Copaipo, Chili," "On the Analysis of a Surface Soil from the Desert of Atacama," "On the Action of Heat on Oxychloride of Copper," "On Algodonite, a New Mineral, containing Arsenic and Copper," "On the Separation of Iodine, Bromine, and Chlorine, with some Analyses of their Combinations with Silver in Chili," "On the Action of Hydrochloric Acid on Sulphate of Mercury, in the Presence of certain other Substances," "On Some Minerals containing Arsenic and Sulphur from Chili," "On Some Native Combinations of Oxide of Mercury with Oxide of Antimony," "On the General Distribution of Bismuth in Copper Minerals," "Some Results of the Analysis of Commercial Coppers" (joint paper with Abel), "On the Double Sulphides of Copper and Iron," "On the Existence of Silver in Sea-Water," "On the Separation of Iron from Manganese," "On the Cuprous Oxide of Manganese from Chili," "On the Artificial Formation of Atacamite," "On Various Methods for the Estimation of Copper," "On the Double Arseniate of Magnesia and Ammonia," "On Ludlamite, a New Mineral," "On a Brittle Variety of Silver from Bolivia," &c.

James Higgin was the fourth son of Thomas Housman Higgin, of Greenfield, Lancaster, by his wife, Sarah, daughter of the Rev. James Winfield, M.A., of Chester. He was of an old Lancashire stock, his father's family having been settled since the latter part of the fifteenth century on a small property near the town of Colne, in Lancashire. He was born in the year 1824, in Lancaster Castle, of which his father was then governor. His education was commenced at the Lancaster Grammar School, and subsequently he studied under the Rev. James Wheeler. He left Lancaster in 1839, and went to Horwich Vale Print Works (the property of his uncle, Mr. Thomas Chippendale), where he remained until the business was given up about 1846. He next went to Manchester, where he worked in the laboratory of Dr. Angus Smith. While he was at Horwich Vale, he commenced an elaborate investigation of the constituents of madder. The work was finished during the time that he was with Dr. Angus Smith, and in 1848 he published a paper in the *Philosophical Magazine* (**33**, 282—294) with a view of showing that Dr. Schunck's assertion that madder owed the whole of its tinctorial power to alizarin was incorrect. Dr. Schunck had described madder as consisting "of three principles, xanthine, a yellow; rubiacine, an orange; and alizarine, a red colouring matter," and said that the two former were valueless for colouring purposes. Mr. Higgin showed that extract from madder undergoes a remarkable spontaneous transformation when allowed to stand, inasmuch as the alizarin increases in quantity owing to the decomposition of the other constituents. He considered that this was a development closely akin to fermentation, for he found that the change proceeded most rapidly at temperatures from 120—130° F. He, therefore, stated his belief in the theory advanced by Decaisne that all the colouring matter of madder arises primarily from xanthin, especially as fresh madder roots contain only a deep yellow fluid. It has since been ascertained that madder contains a ferment to which the name of erythrozym has been given. The publication of this paper was the means of bringing Mr. Higgin into connection with Dr. Schunck, who admitted the correctness of Mr. Higgin's views, and owned himself wrong. From this time, up to 1850, Mr. Higgin remained in Dr. Schunck's works at Rochdale, when his principal study was the manufacture and use of tin salt. In 1850, he entered into partnership with Mr. Nathan Lloyd, and carried on an extensive business as a chemical manufacturer. On the retirement of Mr. Nathan Lloyd, his brother Abraham took his place, and the business was carried on under the name of James Higgin and Co., until 1874, when it was changed to Higgin, Lloyd, and Co. Mr. Higgin's practical experience of the wants of dyers and calico-printers peculiarly fitted

him for the work of manufacturing chemicals and dyes for them, and his extensive knowledge and inventive genius combined to make the business a success. Although Mr. Higgin did not publish many papers, the amount of chemical work which he did was very large. He was the author of the article on Calico Printing in Ure's Dictionary. In 1850 he published a paper in the *Chemical Gazette* (8, 249—250), on a qualitative test for nitric acid. In 1881, together with his son Alfred J. Higgin, he took out a patent for an electric battery, in which tin is substituted for zinc. In this way, the refuse from the battery can be used for making tin salt. Mr. Higgin died on June 21st, 1885, at his residence, The Hollies, Timperley, near Manchester, and was interred at Kersal, near to his old friend Dr. Angus Smith.

He was elected a fellow of the Chemical Society in 1852.

Mr. Alfred Tribe was born in London in the year 1839, in humble circumstances, and his first acquaintance with science seems to have been obtained as a boy at the Royal College of Chemistry. While waiting upon the students there, he acquired whatever knowledge he could, and repeated at home many of the experiments he had seen them perform. Dr. Hofmann, pleased with his desire for knowledge, gave him every encouragement and assistance in his power. In 1855, at the age of 16, he became the assistant of Dr. Medlock, then of Dr. Forbes Watson, and afterwards assisted Prof. Williamson, of University College. He then went to Dr. Bernays, who in 1862 induced him to spend a year at Heidelberg under Prof. Bunsen, and kept his place at St. Thomas's Hospital open for him while he was away. On his return, he continued to act as laboratory assistant and Demonstrator of Chemistry.

In 1865 he became the private assistant of Dr. Gladstone, and remained head of the laboratory till his death. From 1877 he held the Lectureship on Metallurgy to the Medical School of the National Dental Hospital, and since 1874 he was Lecturer on Chemistry and Director of Practical Chemistry in Dulwich College.

He became successively a Fellow of the Chemical Society, of the Institute of Chemistry, and of the Society of Chemical Industry.

Mr. Tribe was pre-eminently a scientific investigator. He loved patient and original research, and all his work was most carefully and honestly done. He published a large number of papers principally on the borderland between chemistry and physics. His first paper was on Sulphide of Ammonium, his second on the Expansion of Bismuth at the Freezing Point. His more important inquiries were connected with the agglomeration of copper and the rarer metals by the occlusion of hydrogen, and especially a series of experiments on

the distribution of electricity in an electrolyte traversed by a current. The curious and suggestive results of this investigation appear in abstract in the *Proceedings of the Royal Society* for January and June, 1881, and are most fully expounded in the second edition of Mr. J. E. H. Gordon's "Treatise on Electricity and Magnetism."

His most important research carried on in conjunction with Dr. Gladstone is contained in a series of papers on the Copper-zinc Couple, published principally in the Journal of the Society. He was the first to observe the greatly enhanced chemical power of zinc when covered with spongy copper. He was also the originator of another long series of papers in our Journal on the Aluminium-iodine Reaction, the last of which was read only the night before he was taken ill. His discovery of these two new methods of acting on chemical compounds, led to the discovery of many new substances, including the aluminium alcohols and their products of decomposition.

In addition to these chemical inquiries, they worked together on electrical matters—describing an air-battery, that is, one in which the oxygen of the air took part; some experiments on thermal electrolysis; and, more particularly, the chemistry of Planté's and Faure's secondary batteries. The results of this investigation were collected and published in a separate treatise. Mr. Tribe took out some patents for a new modification of these secondary batteries.

As a teacher of science, Mr. Tribe was very successful. He had the art of communicating his own enthusiasm to his laboratory students, and his practical classes were well attended, although the boys had to give up their Wednesday half-holidays for that purpose. Many of these students have distinguished themselves since at the Universities or elsewhere.

At these pursuits, Mr. Tribe worked earnestly and continuously, being little known personally beyond his laboratories and his home. His widow, and four surviving children, together with a small circle of intimate friends, will however long remember the thorough uprightness of his character, and the self-denying purpose of his life.

It was moved by Dr. Gladstone, and seconded by Professor Thorpe, that the thanks of the meeting be given to the President for his address, and that he be requested to allow it to be printed. Referring to the publication of the catalogue, Dr. Gladstone said that in looking through it he felt that it not only gave information as to what was, but also what was not, in the library, and it might well serve to lead many of us to make suggestions and to help to fill up gaps from our own shelves. The resolution was unanimously accepted, and was acknowledged by the President.

The Treasurer, Dr. Russell, then read his report, giving an explanation of the balance sheet. He said that the funds of the Society were in a satisfactory state, the income for the year having been £3743 and the expenditure £3108, leaving a balance in hand of £635, a sum that would make it possible to fund the life compositions received during the year.

Mr. Carteighe moved that the thanks of the Society be tendered to the Treasurer for his services during the past year; this was seconded by Mr. Friswell.

M. Crookes proposed a vote of thanks to the auditors, which was seconded by Professor Clowes; Mr. Makins replied.

A vote of thanks to the Officers and Council having been proposed by Mr. H. B. Dixon, seconded by Mr. Pickering, and acknowledged by Dr. Armstrong,

Mr. Howard moved that the thanks of the meeting be given to the Editor, Sub-editor, Abstractors and Librarian for their important services to the Society during the year; this was seconded by Mr. J. A. R. Newlands. Mr. Groves and Dr. Thorne replied.

Professor Humpidge and Dr. Teed were appointed scrutineers, and a ballot having been taken, the following were declared to be elected as Officers and Council for the ensuing year:—

President: Dr. Hugo Müller.

Vice-Presidents who have filled the office of President: Sir F. A. Abel; Dr. Warren De La Rue; Prof. Frankland; Dr. J. H. Gilbert; Dr. J. H. Gladstone; Professor A. W. Hofmann; Professor W. Odling; Dr. W. H. Perkin; Sir Lyon Playfair; Sir H. E. Roscoe; Professor A. W. Williamson.

Vice-Presidents: Mr. W. Crookes; Professor J. Dewar; Mr. David Howard; Professor G. D. Liveing; Professor T. E. Thorpe; Professor W. A. Tilden.

Secretaries: Dr. H. E. Armstrong; Mr. J. Millar Thomson.

Foreign Secretary: Dr. F. R. Japp.

Treasurer: Dr. W. J. Russell.

Ordinary Members of Council: Messrs. H. T. Brown; Professor T. Carnelley; M. Carteighe; Professor Frank Clowes; A. E. Fletcher; R. J. Friswell; Professor R. Meldola; R. Messel; J. A. R. Newlands; S. U. Pickering; Professor W. Ramsay; Thomas Stevenson.

DR. THE TREASURER IN ACCOUNT WITH THE CHEMICAL SOCIETY FROM MARCH 23, 1885, TO MARCH 22, 1886. CR.

	£	s.	d.	£	s.	d.
Balance at Bank March 23rd, 1885	1,218	8	0			
,, in hands of Treasurer	1	13	4			
				1,220	1	4
Receipts by Admission Fees, Subscriptions, and Life Compositions, from March 23rd, 1885, to March 22nd, 1886.						
23 Life Compositions	440	0	0			
109 Admission Fees	436	0	0			
2 Subscriptions for 1882	4	0	0			
23 ,, ,, 1883	46	0	0			
72 ,, ,, 1884	143	0	0			
319 ,, ,, 1885	629	0	0			
719 ,, ,, 1886	1,352	0	6			
1 ,, ,, 1887	2	0	0			
				3,052	0	6
Sale of Journal and Index				340	9	8
Subscriptions for Proceedings of Royal Society				43	0	0
,, from Institute of Chemistry				7	10	0
,, from Society of Public Analysts				4	4	0
An unclaimed Dividend on the Dirks Legacy				3	9	5
Contribution from Dr. Gilbert towards expense of printing tables				5	0	0
Dividend on Consols				116	0	0
,, Metropolitan Board of Works 3½ per Cent. Stock				140	11	1
,, London and North Western Railway Debenture Stock				30	10	8
				4,962	16	8

Assets.	£	s.	d.
Balance at Bank	1,529	12	10
,, in hands of Treasurer	0	8	8
Three per Cent. Consols	4,000	0	0
London and North Western Railway Debenture Stock	788	0	0
Metropolitan Board of Works 3½ per cent. Stock	4,300	0	0

	£	s.	d.	£	s.	d.
Expenses on Account of Journal.						
Salary of the Editor	250	0	0			
Salary of the Sub-Editor	100	0	0			
Incidental Expenses of Editor	1	15	0			
Fees to Abstractors	283	10	10			
Periodicals for Abstractors	14	18	6			
Printing of Journal	1,193	8	0			
Distribution of Journal	268	9	2			
				2,112	1	6
Expenses on Account of Library.						
Salary of Librarian	50	0	0			
,, Library Attendant	62	0	0			
Books and Periodicals	53	4	3			
Binding and Boxes for Periodicals	68	7	2			
Honorarium to Mr. Warington and Dr. Thorne for services with regard to new Catalogue	50	0	0			
New Bookcases and alterations to old ones	110	6	10			
Additional Enamel Letters and Numbers	12	18	4			
Library Ladder, &c.	1	14	6			
				408	11	1
Printing Authors' Copies				46	12	0
Distributing Proceedings of Royal Society				3	19	0
Printing Abstracts of Proceedings				80	9	6
Post Cards with Lists of Papers				2	7	4
Miscellaneous Printing				44	7	6
Inhabited House Duty and Income-tax				10	8	9
Stationery, Postage, &c.				46	6	8
Keeping Fire Extinguishing Apparatus in order (four years)				6	4	7
Repairs to Gas-burners, Window Blinds, &c.				9	4	3
Collector's Commission on Subscriptions				152	8	0
Treasurer's Stamps, Clerical Aid, and Drafts				6	1	5
House Expenses.						
Providing Refreshments	22	13	1			
Heating the Building	18	16	0			
Lighting ,,	54	2	3			
Cleaning ,,	20	0	0			
Wages of House Porter	52	0	0			
Petty House Expenses	7	13	5			
Gratuity to Gate Porters	2	2	0			
Repairs	1	3	0			
				178	9	9
Treasurer's Petty Cash Disbursements				0	8	10
Purchase of £300 Metropolitan Board of Works 3½ per cent. Stock				324	15	0
Balance at Bank	1,529	12	10			
,, in hands of Treasurer	0	8	8			
				1,530	1	6
				4,962	16	8

Audited and found correct. { G. H. MAKINS. WYNDHAM R. DUNSTAN.

March 24th, 1886.

THE TREASURER OF THE CHEMICAL SOCIETY IN ACCOUNT WITH THE RESEARCH FUND.
FROM MARCH 23RD, 1885, TO MARCH 22ND, 1886.

DR.

Date		£	s.	d.
1885.	Balance at Bank	209	13	10
July 11.	Subscription from Drapers' Company	105	0	0
	Dividend on North British Railway Stock (three Dividends)	58	3	5
	Dividend on Metropolitan Board of Works Stock	125	6	5
		£498	3	8

CR.

Date		£	s.	d.
1885. July.	Grants made	50	0	0
1886. February.	Grants made	105	0	0
	Balance at Bank	343	3	8
		£498	3	8

Assets.

	£	s.	d.
North British Railway 4 per cent. Stock	1,000	0	0
Metropolitan Board of Works $3\frac{1}{2}$ per cent. Stock	3,700	0	0
Balance at Bank	343	3	8

Audited and found correct,
March 24th, 1886.

G. H. MAKINS.
WYNDHAM R. DUNSTAN.

XXXIV.—*The Relation of Benzalmalonic Acid to its Mononitro-derivatives.*

By CHARLES M. STUART, M.A., Fellow of St. John's College, Cambridge.

IN previous communications (Trans., 1883, **43**, 403; 1885, **47**, 155), I have described benzalmalonic acid and its nitro-derivatives, and remarked on the stability of the orthonitro-derivative as compared with the corresponding para- and meta-derivatives, and with the unnitrated acid. It seemed that if any comparative measure of this stability could be obtained, it would be a useful contribution to the history of isomerism, moreover, the substances seemed well adapted for this study.

When benzalmalonic acid is boiled with water, the following reactions take place :—

$$\text{I. } C_6H_5{\cdot}CH{:}C(COOH)_2 + H_2O = \underset{\text{Benzoic aldehyde.}}{C_6H_5{\cdot}COH} + \underset{\text{Malonic acid.}}{CH_2(COOH)_2}.$$

$$\text{II. } C_6H_5{\cdot}CH{:}C(COOH)_2 = \underset{\text{Cinnamic acid.}}{C_6H_5{\cdot}CH{:}CH{\cdot}COOH} + CO_2.$$

The three nitro-derivatives undergo decomposition in a similar manner, for although I stated in my last communication that the orthonitro-derivative was not decomposed on boiling, I find now that a slight decomposition takes place. The amount of this decomposition was measured by the following method :—

A number of centigrams corresponding with the molecular weight of the acid was boiled with 150 c.c. of water in a flask connected with a reflux condenser, at the upper end of which was a calcium chloride tube and potash apparatus for absorbing carbon dioxide as in organic analysis. In the case of the unnitrated acid, agitation with ether sufficed to remove benzaldehyde, cinnamic acid, and unaltered benzalmalonic acid, leaving malonic acid in solution, which was then determined by means of a seminormal solution of potash, phenolphthaleïn being used as indicator, and a correction made for the solubility of malonic acid in ether.

By this means, the carbon dioxide gave the amount of decomposition according to equation II, and the malonic acid that corresponding to equation I. In the case of the nitrated acid, it was found better to determine directly the amount of aldehyde produced; this was done by neutralising with sodium carbonate, filtering off any precipitated aldehyde, and agitating the filtrate with ether; the ethereal solution

was then dried with calcium chloride and the ether distilled off. The residue, together with the aldehyde collected by filtration, which had in the meantime been allowed to drain on blotting paper, was dissolved in chloroform, and the solution filtered and evaporated in a counterpoised dish, the residue in the dish being allowed to dry in a vacuum over sulphuric acid. In this way remarkably concordant results were obtained.

Benzalmalonic Acid.

		KHO sol.	CO_2.
Boiled for one hour.	I.	31·00 c.c.	undetermined.
	II.	31·22 ,,	0·0476 gram.
	III.	30·72 ,,	0·0469 ,,
Boiled for 15 minutes.	I.	21·05 ,,	0·0062 ,,
	II.	21·20 ,,	0·0055 ,,

A solution of malonic acid in water being made of approximately the same strength, on agitation with the same amount of ether, it was found that the ether dissolved $\frac{1}{11}$ part of the malonic acid in solution, $\frac{1}{10}$ of the number of c.c. of KHO are therefore to be added in each experiment.

Paranitrobenzalmalonic acid.

		Paranitrobenzaldehyde.	CO_2.
Boiled for one hour.	I.	1·2120 gram.	0·6550 gram.
	II.	1·2495 ,,	0·0548 ,,
Boiled for 15 minutes.	I.	0·9293 ,,	0·0170 ,,
	II.	0·9458 ,,	0·0166 ,,

Metanitrobenzalmalonic Acid.

		Aldehyde.	CO_2.
Boiled for one hour.	I.	1·2551 gram.	0·0458 gram.
	II.	1·2069 ,,	0·0634 ,,
	III.	1·2043 ,,	0·0554 ,,
Boiled for 15 minutes.	I.	0·9266 ,,	0·0280 ,,
	II.	0·9446 ,,	0·0256 ,,

Orthonitrobenzalmalonic Acid.

		Aldehyde.	CO_2.
Boiled for one hour.	I.	(9·8 c.c. $\frac{n}{2}$ KHO sol. used).	0·0252 gram.
	II.	0·3571 gram.	0·0287 ,,
	III.	0·3692 ,,	0·0232 ,,
Boiled for 15 minutes.	I.	0·1314 ,,	0·0050 ,,
	II.	0·1315 ,,	0 0055 ,,

	Boiled for 1 hour. Decomposition according to			Boiled for 15 min. Decomposition according to		
	Equation I.	Equation II.	Total.	Equation I.	Equation II.	Total.
Benzalmalonic acid	85·2	—	—	57·8	1·41	59·2
" "	85·8	10·8	96·6	58·3	1·25	59·55
" "	84·4	10·6	95·0	—	—	—
Paranitrobenzalmalonic acid	80·2	14·8	95·0	61·54	3·89	65·4
" "	82·7	12·4	95·1	62·64	3·77	66·4
Metanitrobenzalmalonic acid	83·1	10·4	93·5	61·3	6·3	67·6
" "	79·9	14·4	94·3	62·5	5·8	68·3
" "	79·7	12·6	92 3	—	—	—
Orthonitrobenzalmalonic acid	24·5	5·7	30·2	8·70	1·18	9·88
" "	23·6	6·5	30·1	8·71	1·25	9·96
" "	24·4	6·4	30·8	—	—	—

Bromine Additive Products.

Another important difference between the orthonitro-acid on the one side, and the unnitrated acid with its para- and meta-nitro-derivatives on the other, is in the behaviour of these compounds when treated with bromine, or hydrobromic acid. The combined bromine was estimated by heating the substance with lime, dissolving in nitric acid, adding to the filtered solution a known quantity of decinormal solution of silver nitrate, and estimating the excess of silver by means of decinormal thiocyanate solution.

Benzalmalonic Acid and Hydrobromic Acid.

Benzalmalonic acid was placed in concentrated hydrobromic acid, allowed to remain for two or three days, and then filtered through a platinum cone; it was freed from excess of hydrobromic acid by being placed under a bell-jar with solid potash. A white amorphous powder was left, which on analysis gave the following results:—

0·2742 gram substance required 10·7 c.c. $\frac{n}{10}$ $AgNO_3$ solution.

= 29·09 per cent. Br. Theory.... 29·30.

The substance, therefore, has the formula of phenyl-bromisosuccinic acid, $C_6H_5{\cdot}CHBr{\cdot}CH(COOH)_2$.

It cannot be purified, as when treated with water it dissolves,

and in a few minutes a turbidity appears in the liquid which increases until a mass of crystals of cinnamic acid is formed, whilst the solution is found to contain hydrobromic acid, the change being expressed by the equation $C_6H_5{\cdot}CHBr{\cdot}CH(COOH)_2 = C_6H_5{\cdot}CH:CH{\cdot}COOH + CO_2 + HBr$. On treating this acid with alcohol, it dissolves readily, and on allowing the alcohol to evaporate, benzalmalonic acid is left, the alcohol having removed HBr.

Benzalmalonic Acid and Bromine.

Benzalmalonic acid was suspended in chloroform and an amount of bromine equivalent to 1 mol. added; the liquid became slowly decolorised. The deposit was collected, washed with chloroform, and analysed.

0·4235 gram required 22·6 $\frac{n}{10}$ $AgNO_3$ solution.

= 42·62 per cent. Br. Theory .... 43·18.

It is, therefore, phenyldibromisosuccinic acid,

$$C_6H_5{\cdot}CHBr{\cdot}CBr(COOH)_2.$$

It melts at 96°, with evolution of hydrogen bromide, leaving a residue which again becomes liquid with effervescence at 130—140°.

On treatment with water, it at once dissolves, but in a few minutes the solution becomes turbid, and the α-bromocinnamic acid described by Claisen, m. p. 131°, is deposited. The reaction being—

$$C_6H_5{\cdot}CHBr{\cdot}CBr(COOH)_2 = C_6H_5{\cdot}CH:CBr{\cdot}COOH + CO_2 + HBr,$$

In experimenting with ethyl benzalmalonate, I was surprised to find one carefully distilled specimen crystallised in large transparent crystals, melting at 32°. Claisen mentions it as an oil, and I had not previously observed the crystallisation.

0·471 gram gave 0·277 gram H_2O and 1·1637 gram CO_2.

	Found.	Theory.
C	67·38	67·74
H	6·53	6·45

This ethyl salt was treated with hydrobromic acid, but the product obtained was an oily substance which could not be purified sufficiently for analysis.

Metanitrobenzalmalonic Acid and Hydrobromic Acid.

This acid behaves in exactly the same way as the unnitrated acid, a white amorphous residue is obtained, of which on analysis—

$$0 \cdot 2722 \text{ gram required } 8 \cdot 45 \ \frac{n}{10} \text{ Ag.}$$

Found .. 24·83 per cent. Br. Theory .. 25·15

It is, therefore, metanitrophenyl-β-bromisosuccinic acid.

It is decomposed by water with the formation of metanitrocinnamic acid, and by alcohol with the formation of metanitrobenzalmalonic acid in the same way as the derivative of the unnitrated acid described above.

Metanitrobenzalmalonic Acid and Bromine.

Metanitrobenzalmalonic acid was suspended in chloroform, and an amount of bromine equivalent to 1 mol. added, the solution became decolorised, and the residue after being washed with chloroform was analysed.

$$0 \cdot 4714 \text{ gram required } 23 \cdot 9 \text{ c.c. } \frac{n}{10} \ AgNO_3 \text{ solution.}$$

= 40·56 per cent. Br. Theory .. 40·30

It is, therefore, metanitrophenyldibromisosuccinic acid. When heated, it gives off hydrogen bromide at 120—140°, and melts with effervescence at 195°. It dissolves in water, and the solution quickly becomes turbid and deposits white crystals melting at 212°, of which on analysis—

$$0 \cdot 3674 \text{ gram required } 13 \cdot 6 \ \frac{n}{10} \ AgNO_3 \text{ solution.}$$

	Theory for metanitro-α-bromocinnamic acid.
= 29·85 per cent.	29·41

It is, therefore, metanitro-α-bromocinnamic acid.

Ethyl metanitrobenzalmalonate, m. p. 73°, dissolved in concentrated hydrobromic acid, and after a time the solution deposited crystals which were collected and recrystallised from bisulphide of carbon; on analysis—

$$0 \cdot 376 \text{ required } 10 \cdot 4 \text{ c.c. } \frac{n}{10} \ AgNO_3 \text{ solution.}$$

= 22·12 per cent. Br. Theory .. 21·39 per cent.

It has the formula $C_6H_4(NO_2)\cdot CHBr\cdot CH(COOC_2H_5)_2$, and is tolerably stable, as it can be melted (m. p. 88°) or crystallised without undergoing alteration, and is not decomposed by water.

Paranitrobenzalmalonic Acid and Hydrobromic Acid.

When paranitrobenzalmalonic acid is placed in concentrated hydrobromic acid, a residue is obtained which can be freed from water and hydrobromic acid by being placed under a bell-jar with potash. On analysis—

0·8793 gram gave 0·5261 AgBr.

= 25·46 per cent. Br. Theory .. 25·15

It dissolves in water, and the solution rapidly becomes turbid and deposits paranitrocinnamic acid, m. p. 286°; with alcohol it gives para-nitrobenzalmalonic acid.

Paranitrobenzalmalonic Acid and Bromine.

If paranitrobenzalmalonic acid is suspended in chloroform, and an amount of bromine equivalent to one molecule added, the colour of the solution becomes gradually paler, but is not entirely decolorised. The deposit, after being collected and washed with chloroform, appears to be a mixture of the paranitrobenzalmalonic acid with its dibrominated derivative, as the percentage of bromine found was always low, and the substance was only partially dissolved by water, with subsequent deposition of crystals. Paranitrobenzalmalonic acid is insoluble in chloroform, and is only partly converted into the bromo-additive product by the above method. The action of bromine itself on the acid was then tried. A specimen of paranitrobenzalmalonic acid was placed in bromine in a stoppered cylinder, which was frequently shaken, and at the end of a month chloroform was added, and the mixture filtered. The residue was then washed with chloroform and allowed to dry; it gives off hydrogen bromide at 90—100°, and the residue melts with effervescence at 188°; the residue left melts at 250—260°.

On analysis—

0·5256 gram required 26 8 c.c. $\frac{n}{10}$ $AgNO_3$ solution.

= 40·79. Theory.... 40·30

it is therefore paranitrophenyldibromisosuccinic acid. On treating it with water, it dissolves, and the solution deposits needles melting at 208°. Of these—

0·1402 gram required 5·17 c.c. $\frac{n}{10}$ $AgNO_3$ solution.

= 29·50. Theory .. 29·41

The substance, therefore, is the paranitro-α-bromocinnamic acid, described by Muller (*Annalen*, **212**, 122) as the β-acid.

Ethyl paranitrobenzalmalonate dissolves in concentrated hydrobromic acid, and the solution deposits crystals. These, after being washed with water and crystallised from bisulphide of carbon, were analysed :—

0·4208 gram required 11 c.c. $\frac{n}{10}$ $AgNO_3$ solution.

= 20·95 per cent. Br. Theory .. 21·39

It is therefore ethyl paranitrophenyl-β-bromisosuccinate. It melts at 89°, and is stable, as it can be crystallised from alcohol or bisulphide of carbon, or washed with water without alteration.

Addition-products of Orthonitrobenzalmalonic Acid.

Orthonitrobenzalmalonic acid behaved quite differently from the compounds above described. If placed in concentrated hydrobromic acid, a yellow substance was deposited, and a further quantity of the same compound was obtained on diluting the liquid. It was not decomposed or dissolved by water, and is insoluble in benzene, ether, chloroform, and bisulphide of carbon. It dissolves readily in alcohol, but could not be obtained crystallised. It melts without effervescence at about 227°. Two analyses gave—

No. I.	41·69	per cent. Br.
No. II.	41·74	,, ,,

Theory for additive compound with HBr similar to the others, 25·15 per cent.

A similar compound is obtained when orthonitrobenzalmalonic acid is treated with chloroform and bromine.

Ethyl orthonitrobenzalmalonate dissolves in concentrated hydrobromic acid, and the solution deposits crystals, which after being collected, washed with water, and crystallised from bisulphide of carbon, were submitted to analysis.

0·4729 gram required 12·77 c.c. $\frac{n}{10}$ $AgNO_3$ solution.

= 21·60 per cent. Br. Theory .. 21·39

It is orthonitrophenyl-β-bromisosuccinate. It melts at 68°, and can be crystallised from the usual solvents; it is not decomposed by water.

The following is a list of the bromo-additive compounds described :—

Benzalmalonic acid + HBr......	Additive product.	Decomposed by water, forming cinnamic and nitrocinnamic acids. Decomposed by alcohol, forming benzalmalonic acid.
p-Nitrobenzalmalonic acid + HBr	Do.	
m-Nitrobenzalmalonic acid + HBr	Do.	
o-Nitrobenzalmalonic acid + HBr	Condensation product.	Not decomposed by water or alcohol.
Benzalmalonic acid + Br_2.......	Additive product.	Decomposed by water, forming *a*-bromocinnamic acids, give off HBr at 100—130°, leaving a residue melting with evolution of CO_2.
p-Nitromalonic acid + Br_2......	Do.	
m-Nitromalonic acid + Br_2......	Do.	
o-Nitromalonic acid + Br_2.......	Condensation product.	Not decomposed by water or alcohol.
Ethyl-*p*-nitrobenzalmalonate + HBr	Additive product.	Stable compounds not decomposed by water, crystallised from alcohol or CS_2.
Ethyl-*m*-nitrobenzalmalonate + HBr	Do.	
Ethyl-*o*-nitrobenzalmalonate + HBr	Do.	

These experiments confirm a statement of Müller (*Annalen*, **212**, 122), that the ethyl salt of an unsaturated acid exhibits a greater tendency to take up bromine and pass into a saturated compound than the acid itself.

I believe that these experiments may contribute something to our ideas as to the structure of benzene. The two symbols which at present claim to represent the structure of benzene are Kekulé's hexagon and Ladenburg's prism. In the former, the carbon-atom in the ortho-position is directly connected with the first carbon-atom, whilst those in the para- and meta-positions are indirectly connected with it; in the latter the carbon-atoms in the para- and meta-positions are directly connected with the first carbon-atom, whilst the carbon-atom in the ortho-position is indirectly connected with it. In Körner's modified hexagon, which is, however, now rejected as showing only two di-derivatives, the carbon-atoms in the ortho- and para-positions are directly connected with the first carbon-atom, and that in the meta-position is indirectly connected with it. Now assuming that a nitro-group attached to one carbon-atom is more likely to modify the stability of a hydrocarbon chain attached to a carbon-atom which is directly connected with it, more so than if that carbon-atom is indirectly connected with it, we should expect to trace out analogies in the following way:—

According to Ladenburg's prism, the para- and meta-nitro-deriva-

tives would behave similarly on the one hand, whilst the ortho-derivative and the unnitrated acid would behave similarly on the other; if the influence of the nitro-group be protective, the para- and meta-derivatives should be more stable.

According to Kekulé's hexagon, the para- and meta-derivatives and the unnitrated acid would behave similarly on the one hand, and the ortho-derivative would behave differently on the other; if the influence of the nitro-group be protective, the ortho-derivative should be more stable than the other three.

According to Körner's modified hexagon, the ortho- and para-derivatives should behave similarly on the one hand, and the meta-derivative and the unnitrated acid should behave similarly on the other; if the influence of the nitro-group be protective, the ortho- and the para-derivatives should be more stable.

We see that of these three hypotheses, the second is the one with which the results obtained are in accord, and I would suggest this as an argument in favour of Kekulé's hexagonal formula.

The words of R. Meyer (*Ber.*, **15**, 1826) in defence of the prism formula against Körner's modified hexagon, are worth quoting in this connection. He says, "It is assumed that the actual relationship of the benzene compounds points rather to analogies between the ortho- and para-derivatives. I do not believe that such an analogy can be recognised."

It was now thought that the action of other aldehydes on malonic acid might also be utilised, with the view of ascertaining if any alteration of stability was produced by altering the side hydrocarbon chain, and I was surprised to find that a derivative of cinnamic aldehyde, containing the double bond twice over, was more stable than any of the compounds mentioned in this paper.

The results obtained are given in the succeeding paper.

XXXV.—*Action of Cinnamic and Salicylic Aldehydes on Malonic Acid.*

By Charles M. Stuart, M.A., Fellow of St. John's College, Cambridge.

A mixture of equal parts of cinnamic aldehyde and malonic acid with half its weight of glacial acetic acid was heated at 100° for six hours; the crystalline product, after being collected and washed successively with glacial acetic acid, water, and chloroform, presented the appearance of yellow needles. On analysis—

0·3639 gram gave 0·8829 gram CO_2 and 0·1446 H_2O.

= H......	4·41 per cent.	Theory......	4·59
C......	66·16 ,,		66·05

It is therefore phenylbutindicarboxylic acid,

$$C_6H_5{\cdot}CH:CH{\cdot}CH:C(COOH)_2.$$

It melts at 208° with effervescence, carbon dioxide being evolved. The residue had no constant melting point, but if a larger quantity was heated at 210° till it ceased to give off carbon dioxide, and the product crystallised from benzene, pure cinnamenylacrylic acid, melting at 165° (Perkin, *Chem. Soc. J.*, **31**, 403), is obtained; the cinnamenylacrylic acid is partially decomposed by heating above 200°.

Phenylbutindicarboxylic acid, unlike benzalmalonic acid, can be boiled with water, without decomposition.

I now tried salicylaldehyde, with the view of ascertaining the influence of a hydroxyl-group in the ortho-position.

A mixture of salicylaldehyde, malonic acid, and glacial acetic acid, on being heated for some time at 100° and allowed to cool, became semi-solid from the formation of crystals. These were drained from acetic acid and recrystallised from hot water, when white needles, melting at 187° without effervescence, were obtained.

On analysis—

I.	0·4347 gram gave	1·0056 gram CO_2 and	0·1288 gram H_2O.
II.	0·3667 ,,	0·8489 ,,	0·1091 ,,
III.	0·3521 ,,	0·8131 ,,	0·1016 ,,

corresponding to—

	I.	II.	III.	Theory. $C_{10}H_6O_4$.
C........	63·09	63·13	62·97	63·15
H.......	3·29	3·30	3·21	3·16

The substance treated with dilute ammonia dissolved, and the solution gave a white precipitate with silver nitrate, of which on analysis—

0·6045 gram gave 0·2211 gram Ag,

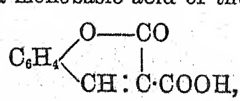
corresponding to 36·57. Theory for $C_{10}H_5O_4Ag$.... 36·36.

The *barium salt* was obtained as a white precipitate on adding barium chloride to the same solution.

0·7117 gram dried at 130° gave 0·3229 gram $BaSO_4$.

= 26·67 per cent. Ba. Theory $(C_{10}H_5O_4)_2Ba$.. 26·60.

This acid is therefore a monobasic acid of the composition



and may be called coumarincarboxylic acid. It is not decomposed by boiling with water, or on melting, but on heating it in a distilling flask above its melting point it evolves carbon dioxide, and at 290° a substance distils over and solidifies in the receiver. When recrystallised, this melts at 67°, and its solution in sodium hydrate gives the characteristic reactions of coumarin with metallic salts. The thermometer then rises rapidly above the boiling point of mercury, and a small quantity of the unchanged coumarincarboxylic acid distils over. An attempt to produce a bibasic hydroxy-acid corresponding to coumaric acid, by heating coumarincarboxylic acid with sodium ethylate, according to Fittig and Ebert's method (*Annalen*, **226**, 351), led to no result.

I am at present occupied with the production of benzalmalonic acid containing some negative element, such as chlorine, in the ortho-position, and hope soon to have the honour of laying my results before the Society.

XXXVI.—*Note on the Action of Ammonia on Chromyl Dichloride.*

By SAMUEL RIDEAL, B.Sc., University College, London.

WHEN the vapour of chromyl dichloride, CrO_2Cl_2, is passed into a vessel containing dry ammonia gas, it takes fire and burns with a white flame, giving, at first, white fumes, and finally a greenish-brown solid. This reaction has been noticed and described by various observers. Liebig thought that the brown compound formed in this manner, and the black compound obtained when chromic chloride, Cr_2Cl_6, is substituted for the chromyl dichloride, consisted of metallic chromium (*Pogg. Ann.*, **21**, 359). Schrötter repeated the experiment with the chromic chloride and analysed the product, which he found to be a nitride of chromium having the formula Cr_3N_4. He did not, however, examine the product of the reaction with chromyl dichloride, but inferred that a compound of similar constitution was formed. He also noticed that this chromium nitride, when heated at 150—200° in a stream of oxygen, took fire and burnt with a red light, evolving nitrogen and oxides of nitrogen. (*Annalen*, **37**, 145). To determine the correctness of Schrötter's inference, a small quantity of the substance obtained from chromyl dichloride was heated in a piece of hard glass tubing and a current of dry oxygen passed through it, but neither nitrogen nor oxides of nitrogen were evolved, and the substance did not glow. It was,

therefore, evident that the compound obtained from chromyl dichloride differed from that derived from chromic chloride.

Thomson also examined the reaction between chromyl dichloride and ammonia, and found that the dark brown solid, when digested with water, left a green powder which was insoluble in nitric acid, and contained chlorine. He also noticed that ammonic chloride was one of the products of the reaction (*Phil. Mag.*, 1827, 452). Persoz, in a paper on the combination of gaseous ammonia with metallic chlorides, has shown that chromyl dichloride combines with ammonia in the ratio of 79·101 of the former to 20·898 of the latter; these numbers give 3 : 8 as the ratio of the reacting molecules.

The present note describes some experiments which were undertaken to correlate and complete these statements. As already mentioned, white fumes are conspicuous at the beginning of the reaction, and when the experiment was conducted in a long tube filled with dry gaseous ammonia, it was noticed that the product was not homogeneous, but consisted of two substances, a volatile white solid, and a non-volatile greenish-brown compound; a current of dry ammonia was passed through the tube for some time after the reaction, so as to ensure the complete decomposition of the chromyl dichloride. The product was then digested with water, in which it was partially soluble; the solution was yellow in colour, contained ammonium chloride, chromic acid, and a substance which could be precipitated as a brown powder by ammonia. This brown precipitate, when boiled with potash, was converted into green chromic hydrate, and the filtrate contained a chromate; it was therefore the brown oxide of chromium, Cr_2O_3,CrO_3. The insoluble residue dissolved slowly in hydrochloric acid, and appeared to consist only of chromic oxide. After being well washed and boiled for some time with water, it contained no chlorine.

It being probable from these results, that some of the ammonia was decomposed with liberation of nitrogen, this gas was looked for among the products. A weighed quantity of the chromyl dichloride in a thin glass bulb was placed in a large and strong glass bottle connected with an apparatus for delivering a rapid current of dry ammonia, and with a delivery tube dipping under mercury. When all the air had been expelled from the apparatus the glass bulb was broken and the gases evolved collected over water. Nitrogen was given off in the proportion of 1 mol. to 3 mols. of chromyl dichloride. In two experiments, the following numbers were obtained :—

Weight of chromyl dichloride.	Volume of nitrogen. Found.	Volume of nitrogen. Theory.
2·0515 grams	96·4 c.c.	98·7
0·5835 ,,	28·6 ,,	28·05

The solid products obtained in these experiments were also collected and analysed. Any uncombined ammonia which might have been condensed on the solid product was removed by passing a current of dry air over it, and after weighing the whole, the amount of ammonia present in a weighed portion was determined. It yielded 22·1 per cent. of combined ammonia, which agrees with the percentage of ammonia (21·9) calculated on the assumption that 8 mols. react with 3 mols. of chromyl dichloride in the following manner:—

$$3CrO_2Cl_2 + 8NH_3 = 6NH_4Cl + CrO_3,Cr_2O_3.$$

The amount of chromic acid in the product was found to be 21·5 per cent. (theory 21·7), and after ignition, the percentage of chromic oxide left was 43·7 (theory 42·7).

The chromyl dichloride, then, in this reaction, appears simply to break up into the dioxide and chlorine, and the latter is then able to react with the ammonia in the ordinary manner. Chromyl dichloride, when heated alone to dull redness, splits up into chromic oxide, oxygen, and chlorine (Wöhler, *Annalen*, **60**, 203), and when heated in a sealed tube loses two-thirds of its chlorine, forming $(CrO_2)_3Cl_2$, proving that the chlorine is only loosely combined. With carbamide, Sell has shown that a compound is formed containing no chlorine (*Proc. Roy. Soc.*, **33**, 267).

The behaviour of chromyl dichloride towards the amines is now being examined.

XXXVII.—*Some Sulphur Compounds of Barium.*

By V. H. Veley, M.A., of the Laboratory, Christ Church, Oxford.

Historical.

Barium Monosulphide.—Berzelius, in his monograph on the sulphides of the alkalis and alkaline earths (*Schweigger's Journal*, **34**, 12), describes the preparation of barium sulphide by the well-known method of subjecting a mixture of barium sulphate and coal to a red heat, lixiviating the mixture, and concentrating by evaporation. A purer product (*Lehrbuch*, **2**, 137) was obtained by heating the oxide or carbonate in an atmosphere of carbon disulphide, a method found by Schöne to give quantitative results.

Barium Hydroxyhydrosulphide.—The composition of the crystals obtained by lixiviating with water the washed mass of barium sul-

phate and coal, and cooling or evaporating the solution, was examined by Röse (*Pogg. Ann.*, **55**, 415), who noted the variation in composition and appearance of the crystals with the conditions of preparation, such as temperature, time of contact of crystals with solution, quantity of water used. By treating barium trisulphide with water and evaporating in a vacuum, Schöne (*Pogg. Ann.*, **112**, 193) obtained successively crystals of barium hydroxyhydrosulphide, $BaSH{\cdot}OH,5H_2O$, the hydrosulphide (*vide infra*), and a tetrasulphide with variable quantities of water of crystallisation.

Barium Hydrosulphide.—Berzelius (*Pogg. Ann.*, **6**, 441) describes the preparation of the crystalline hydrosulphide by saturating a solution of the oxide in water with hydrogen sulphide, adding alcohol to the solution, filtering off the sulphur and oxidised products, and cooling to $-10°$, when groups of four-sided prisms separated; and secondly, by evaporating the solution in a vacuum, when opaque, probably effloresced, acicular crystals were obtained. No analytical results are given, but the quantitative test was applied of the precipitation of manganese sulphide and evolution of hydrogen sulphide on addition of a solution of a manganese salt to a solution of the crystals.

The crystals obtained by Schöne gave on analysis results corresponding to a formula $Ba_4S_7,25H_2O$, but it is admitted that the crystals, which were of a pale-yellow colour, were slightly impure. The crystals lose water at 100—110°, at 230° evolve hydrogen sulphide, and are not completely decomposed into the monosulphide and hydrogen sulphide even at 280—300°.

The sulphides of barium have been examined from a thermochemical point of view by Sabatier (*Ann. Phys. Chem.* [5], **22**, 598).

Barium Thiocarbonate.—Berzelius (*Pogg. Ann.*, **6**, 244) describes this salt as a yellow crystalline substance, sparingly soluble in water.

The preparation of anhydrous barium monosulphide, crystalline barium hydrosulphide, and the conditions of formation of barium thiocarbonate, form the principal subjects of the present communication.

Preparation of Barium Monosulphide, BaS.

The method adopted for the preparation of this substance consisted in passing hydrogen sulphide over a known weight of barium hydroxide, collecting the water evolved, and weighing the resultant barium sulphide.

For this purpose, it was thought especially desirable to obtain the hydroxide in a state of purity, which was effected by the following method:—Recrystallised barium chloride was dissolved in water, and a few drops of ammonia and ammonium sulphide added to

the solution. The small quantity of sulphide of iron precipitated was removed by filtration, the solution was then evaporated to dryness, and the barium chloride rubbed up frequently with absolute alcohol to dissolve out any strontium or calcium chloride, with which the substance is likely to be contaminated. In order to convert the chloride into the hydroxide, the method proposed by Mohr and found successful by Bloxam was used, which consists in outline of boiling the barium chloride with sodium hydrate solution (sp. gr. 1·00—1·15). The sodium hydrate used was purified by solution in alcohol, and in order to eliminate as far as possible the presence of carbonic anhydride and consequent formation of barium carbonate, the process was conducted in vessels filled with hydrogen. The crystals of $Ba(OH)_2,8H_2O$ were recrystallised several times, always in an atmosphere of hydrogen, finally thrown on a filter, and washed with cold, recently boiled water, until the wash-water gave no precipitate with silver nitrate. The crystals thus obtained contained no carbonate. They were then dried over a mixture of potassium hydrate and calcium chloride, and before treatment with hydrogen sulphide, were heated in a current of hydrogen at about 80°, until their weight was constant. The composition of the substance was found to be $Ba(OH)_2,H_2O$, as noticed by previous observers.

	Found.	Theory.
Ratio of $\dfrac{Ba(OH)_2H_2O}{BaO}$	1·227	1·231

It is generally stated in the text-books that crystalline barium hydrate melts in its water of crystallisation at 100°. Experiments, however, showed that the temperature is 83—85°; mean of observations made (i) by enclosing some of the substance in a capillary tube filled with hydrogen, and heating in a bath of glycerol; (ii) by immersing a thermometer into a considerable quantity of the substance heated in a small test-tube, through which a continuous current of hydrogen was passed.

The apparatus used for the conversion of the hydroxide into the sulphide was identical with that described in my paper on some sulphur compounds of calcium (Trans., 1885, 481).

Methods of Analysis used.—Sulphur was determined by Carius' method. Barium was estimated by evaporating the substance with dilute sulphuric acid in a porcelain crucible and weighing the sulphate formed, and water by heating the substance in hydrogen, or preferably in carbonic anhydride, owing to the retention of water by barium hydroxide.

Preliminary experiments indicated that the sulphur compound obtained on heating the monohydrate of barium hydroxide in hydrogen

sulphide retained, at temperatures above 160°, some hydrogen sulphide, which is given off again at a higher temperature; it is only by prolonged heating at 200° that the conversion of the hydroxide into the monosulphide can be completed.

The change was investigated both by synthetical and analytical methods.

Synthesis.

Conditions of experiment.	Temperature.	Time.	Weight of material.	Difference.	Water collected.
			grams.	grams.	grams.
Hydrate of barium hydroxide	—	—	2·1484	—	—
Heated in a current of hydrogen sulphide	85°	6 hrs.	2·5484	+0·400	+0·3539
Heated in a current of hydrogen	95	4 hrs.	2·3374	−0·211	+0·1775
" "	"	"	2·3104	−0·027	+0·0278
" "	120—125	"	2·1868	−0·1236	+0·058
" "	130—135	"	2·1798	−0·007	nil.
" "	200—205	"	1·9348	−0·245	"
" "	"	"	1·9338	−0·001	—
Barium sulphide	—	—	1·9338	—	0·6172

Analysis of Resultant Substance.

	Percentage found.	Theory for BaS.
Sulphur as barium sulphate, by Carius' method	18·76	18·94
Barium as barium sulphate....	81·05	81·06
	99·81	100·00

Synthesis.

	Theory.	Experiment.
Hydrate of barium hydroxide, $Ba(OH)_2,H_2O$	2·1484	2·1484
Barium sulphide, BaS obtained	1·9234	1·9338
Water collected..............	0·6147	0·6172

A similar series of experiments were conducted, but owing to an accident, the determination of water was lost.

SERIES II.

Conditions of experiment.	Time.	Temperature.	Weight of material.	Difference.
Hydrate of barium hydroxide	—	—	grams. 1·838	grams. —
Heated in a current of hydrogen sulphide	{ 2 hrs. 6 hrs. }	{ 15·20° 100—110 }	1·9225	+0·0878
Heated in a current of hydrogen	14 hrs.	155—160	1·772	−0·1535
,, ,, ...	3 hrs.	200—210	1·6597	−0·1023
,, ,, ...	,,	210—215	1·66	−0·0097
,, ,, ...	,,	,,	1·6505	−0·0098
,, ,, ...	,,	,,	1·650	−0·0005
Barium sulphide	—	—	1·650	—

Analysis of Resultant Substance.

	Percentage found.	Theory for BaS.
Sulphur	19·04	18·94
		81·06
		100·00

Synthesis.

	Theory.	Experiment.
Hydrate of barium hydroxide ..	1·838	1·838
Barium sulphide	1·643	1·650

Thus both by synthetical and analytical processes it is shown that the hydrate of barium hydroxide is converted into barium sulphide in accordance with the equation—

$$Ba(OH)_2,H_2O + H_2S = BaS + 3H_2O.$$

Anhydrous barium sulphide, which apparently has not previously been described, is a white amorphous powder, soluble in water, but perhaps only after decomposition into the hydroxide and hydrosulphide. On exposure to air, it changes to a pale yellow, and then to an orange colour, owing to the formation of oxidised products. On addition of concentrated nitric acid, its heat of oxidation is so great that it becomes vividly incandescent. If it contains a trace of iron, the sulphide is of a pale pink colour, but with a larger excess it has the same colour as ordinary fresh lime.

Lixiviation of Anhydrous Barium Sulphide with Water.

It is well known that when anhydrous barium sulphate, obtained by the reduction of the sulphate with coal or other carbonaceous matter, is heated with an excess of water, it is decomposed completely into the hydrosulphide, which dissolves, and the hydroxide, which in part dissolves, in part crystallises out. But if a smaller quantity of water be added, six-sided tables of barium hydroxyhydrosulphide separate, admixed with variable proportions of the hydroxide. As the writer had occasion to prepare a considerable quantity of the former substance, and as no details have been given regarding the time of boiling, the quantity of water used for lixiviation of the material, &c., a series of comparative experiments were made to determine the best conditions. In each experiment the following quantities were used :—

Barium sulphate	150 grams.
Coal	50 ,,
Starch	10 ,,

These were well mixed and heated in a crucible to a red heat for one hour. In order to equalise the conditions as far as possible, the materials were always taken from the same sample, the same crucible and lid were used, and the roasting performed at the same time of day, when the pressure of gas supplied was the same. After cooling, the roasted mass was placed in a flask, and variable quantities of boiling water poured upon it, the whole being boiled for four minutes. It was then rapidly filtered and cooled, the vessel being well agitated to promote the separation of crystals. The crystalline deposit was allowed to stand until the supernatant liquor was perfectly cool, collected, washed once with alcohol to remove the adherent solution of the hydrosulphide, and dried between folds of blotting-paper. Though the results are of course not rigidly comparable, yet they are sufficient to show both the variation of yield, and of the proportion of barium sulphide contained therein, with the proportion of water used for the crystallisation.

Volume of water.	Weight of crystals.	Percentage of barium sulphide in crystals.
250	42 grams	43·1
300	58 ,,	41·13
300	56 ,,	42·48
350	39 ,,	28·90
400	10 (barium hydroxide)	nil.
450	nil.	nil.

These crystals owing to their ready oxidisability do not offer a con-

venient material for the preparation either of the anhydrous sulphide or of the hydrosulphide.

Barium Hydrosulphide, $Ba(SH)_2,4H_2O$.

To prepare this substance, the method described by Divers (Trans., 1884, 271) for the corresponding calcium compound was used with suitable modifications. In the preparation tube, a solution of the crystalline barium hydroxide, saturated at 100°, was made in a continuous current of hydrogen, which was then replaced by hydrogen sulphide purified from oxygen and dried. A considerable development of heat accompanied the absorption of the gas. To obtain a saturated solution, the hydroxide dried at 100°, or preferably the anhydrous oxide was added, the solution being kept at a temperature of 60—70°, while a continuous current of hydrogen sulphide was passed in. This process requires several days for completion. Ultimately crystals separate from the solution when cold. To obtain these free from undissolved impurities such as silica, ferric sulphide, and unaltered oxide, the solution was again warmed to 40°, and the supernatant liquid quickly decanted off into a small stoppered bottle, filled with hydrogen sulphide. The liquid was then cooled, and finally placed in a freezing mixture. Tufts of hard, interlaced acicular crystals separate, which were allowed to grow for some days in the saturated solution. The mother-liquor was drained off, the crystals quickly detached, and dried between folds of blotting-paper, so arranged as to allow of the least possible access of air. When these were dissolved in water and a solution of a manganese salt added, manganese sulphide was precipitated with evolution of hydrogen sulphide; the crystals were insoluble in alcohol. These qualitative tests indicate that the crystals consist of barium hydrosulphide. Their analysis was effected as follows: a weighed quantity was treated according to Carius' method, and from the barium sulphate at first formed was determined the barium and sulphur existing in the form of monosulphide. On filtering and precipitating the filtrate with barium chloride, the sulphur in excess of that required for the monosulphide was determined. If the barium hydrosulphide were perfectly pure these two quantities of barium sulphate should be the same.

Analysis of First Sample.

	Percentage Barium.	Percentage Sulphur.
0·4024 gram gave (i) 0·3334 gram $BaSO_4$..	48·7	11·07 (i)
„ „ (ii) 0·3158 „ ..	—	10·78 (ii)
	48·7	22·15

Atomic ratio of barium to sulphur $= \frac{1}{1{\cdot}95}$.

Analysis of Second Sample.

	Percentage Barium.	Percentage Sulphur.
0·4524 gram gave (i) 0·3861 gram $BaSO_4$..	50·14	11·71
,, ,, (ii) 0·3852 ,, ..	—	11·69
	50·14	23·40

Atomic ratio of barium to sulphur 1 : 1·983.

0·2634 gram heated in a current of carbonic anhydride gave 0·0683 gram water, or 25·92 per cent.

These last results point to a formula, $Ba(SH)_2,4H_2O$, for the crystals.

Percentage results.	Theory for $Ba(SH)_2,4H_2O$.			Found.	
Barium........	49·81			50·14	
Sulphur (i)	11·64	23·28		11·71	23·40
,, (ii)	11·64			11·69	
Water.........	26·18			25·92	
Hydrogen......	0·73		By difference..	0·54	
	100·00			100·00	

The crystals when heated in a sealed capillary tube filled with hydrogen exhibited no signs of liquefaction in their water of crystallisation, but were simply dehydrated, a result in accordance with the observations of Berzelius.

Temperature of Decomposition of Barium Hydrosulphide.

The following experiment was made to test the accuracy of Schöne's statement that the hydrosulphide does not evolve hydrogen sulphide at temperatures below 260°. A weighed quantity of the hydrosulphide in a porcelain boat, enclosed within a piece of combustion tubing, was heated in an air-bath in a current of hydrogen, the gas being purified successively by chromic acid, sulphuric acid, potash, damp oxide of iron, and finally dried with calcium chloride. At the outlet of the U tube containing the damp oxide, a small slip of paper moistened with lead acetate was placed. The gas after passing over the hydrosulphide was passed into a Liebig's bulb apparatus, filled - the lead syrup used for the estimation of sulphur compounds in ch and placed upon a sheet of white paper. The air-bath was

provided with a thermometer enclosed within a similar piece of combustion tubing in order to make its surroundings and temperature identical with that of the hydrosulphide. A blank experiment showed that no coloration was given to the lead solution on passing the hydrogen through the apparatus for one hour. The crystals were then introduced, and the hydrogen passed for a short time, before connecting the bulb apparatus, in order to blow off any hydrogen sulphide liberated by the temporary exposure of the crystals to the carbonic anhydride of the atmosphere. At a temperature of 18°, no decomposition was observed, the lead solution remaining unaltered for half an hour. At a temperature of 50°, the lead solution gradually darkened, thus showing an incipient decomposition; at 55°, the coloration became more marked, while at 60° the lead sulphide was completely precipitated. This decomposition was concomitant with the elimination of water, as at 55° a distinct dew was observed in the cooler portion of the combustion tubing, which increased considerably at 60°. But when the substance is completely dehydrated its stability is remarkably increased, the hydrogen sulphide being retained with great persistence. The results in the following table illustrate the statements above.

Conditions of experiment.	Time.	Temperature.	Weight of substance.	Loss.
$Ba(SH)_2,4H_2O$	—	—	gram. 0·3202	—
Heated in a current of hydrogen	3 hrs.	100—105°	0·2366	0·0836
" " "	"	"	0·2276	0·009
" " "	"	112—115	0 224	0·0036
" " "	{ 1½ hr. 1½ hr.	145—150 170—175 }	0·223	0·001
" " "	3 hrs.	195—200	0·221	0·002
" " "	1½ hr.	235—240	0·221	nil.
" " "	3 hrs.	260—265	0·220	0·001
" " "	"	Red heat	0·1992	0·0198
Loss per cent.	—	—	—	37·85
Loss required by theory for conversion of $Ba(SH)_2,4H_2O$ to BaS	—	—	—	38·18

Thus the hydrogen sulphide is only completely eliminated at a red heat; but at a lower temperature it is evolved slowly as evidenced by a very slight loss in weight, and also by the coloration or precipitation of the lead sulphide from the lead syrup in the course of each of the above experiments, a result which would not have obtained, were the

hydrosulphide accidentally oxidised to the thiosulphate or tetrathionate.

Properties of a Solution of the Hydrosulphide.

A saturated solution of barium hydrosulphide when warm dissolves sulphur with effervescence of hydrogen sulphide, and formation of a dark red liquid. On further addition of sulphur, yellowish-red crystals appear; on pouring the liquid from these, which analysis proved to be a mixture, and allowing the liquid to cool slowly, red crystals separate.

These on analysis gave results corresponding to a formula, $4BaS_4,7H_2O$, probably $BaS_4,2H_2O$ slightly dehydrated, or mixed with a small quantity of the anhydrous tetrasulphide.

	Analysis of crystals.	Calculated for $4BaS_4,7H_2O$.
Barium	46·67 per cent.	46·12
Sulphur........	43·19 ,,	43·27
Water	10·24 ,,	10·61
	100·10	100·00

Atomic ratio of barium to sulphur = 1 : 3·96.

The red solution of barium tetrasulphide is not decomposed by hydrogen sulphide, either at ordinary temperatures or at that of boiling water, differing in this respect from calcium pentasulphide.

Conditions of Formation of Barium Thiocarbonate.

In my former paper on the sulphur compounds of calcium, it was shown that carbon disulphide was absorbed by calcium hydroxyhydrosulphide or the damp sulphide, but not by the anhydrous sulphide or by the hydrosulphide. These conclusions were confirmed by similar experiments with the corresponding barium compounds. Tests were made in which hydrogen, containing a known proportion of carbon disulphide was passed through (i) the solid hydroxide, (ii) the anhydrous sulphide, (iii) a solution of the hydrosulphide, (iv) the crystalline hydroxyhydrosulphide mixed with a large excess of water, (v) the crystalline hydroxyhydrosulphide, and (vi) the mixture of coal and barium sulphide (obtained on roasting the sulphate), slightly damped with water. In experiments (i), (ii), (iii), and (iv), no carbon disulphide was absorbed, and in (v) and (vi) the hydrogen was completely purified from this substance. The negative result obtained in (iv) is explained by the decomposition of the hydroxyhydrosulphide into the hydroxide and the hydrosulphide (the presence of the latter

in the resultant solution being detected by quantitative tests), both of which, taken separately, were shown to be inactive.

The thiocarbonate, as described by Berzelius, is a yellow crystalline solid, adhering firmly to the sides of the containing vessel; it is sparingly soluble in cold, readily soluble in hot water, but is at the same time decomposed. Several attempts were made to obtain this substance in a state fit for analysis, but its preparation presents even greater difficulties than that of the corresponding calcium compound. Alcohol, dilute and absolute, ether and carbon disulphide, were tried as solvents, but without success. Experiments were also made to regenerate barium sulphide from the mixture of thiocarbonate and hydroxyhydrosulphide, obtained by saturating the latter with carbon disulphide vapour; this material was heated to a high temperature in a retort, the air of which was previously replaced by hydrogen. A yellow mass was obtained, which was damped and again tested by passing through it hydrogen containing carbon disulphide; but it was found to be no longer active.

Summary.

The main points of the above paper are as follows:—

(i.) By the action of hydrogen sulphide on the hydrate of barium hydroxide, there is formed barium sulphide and water, in accordance with the equation $Ba(OH)_2,H_2O + H_2S = BaS + 3H_2O$.

(ii.) By the action of hydrogen sulphide on barium oxide in aqueous solution, there is formed a solution of barium hydrosulphide, from which crystals of the composition $Ba(SH)_2,4H_2O$ separate; this substance is far more stable than the corresponding calcium compound.

(iii.) A warm saturated solution of barium hydrosulphide dissolves sulphur to give a red liquid, from which crystals of barium tetrasulphide, probably $BaS_4,2H_2O$, separate.

(iv.) Barium hydroxyhydrosulphide absorbs carbon disulphide with formation of an unstable barium thiocarbonate.

XXXVIII.—*Amidodiphenylsulphonic Acid and Azo-dyes from Diphenyl.*

By Thomas Carnelley, D.Sc., and James Schleselman, University College, Dundee.

In preparing dye-stuffs from diphenyl, either of two methods might be adopted:—

(1.) To combine one of the hydroxydiphenyls, or a sulphonic acid thereof, with a diazo-compound, thus—

$$C_{12}H_8(OH)\cdot N:N\cdot X\cdot SO_3H \text{ or } C_{12}H_7(SO_3H)(OH)\cdot N:N\cdot X, \&c.$$

(2.) To sulphonate amidodiphenyl, diazotise the resulting amidodiphenylsulphonic acid, and combine the diazo-sulphonic acid so obtained with a phenol, amido-compound, &c., thus:—

$$C_{12}H_8(SO_3H)\cdot N:N\cdot X\cdot OH.$$

Attempts to prepare dyes by the former method did not succeed, the yield of hydroxydiphenyl obtained being very small. The second process, however, gave very satisfactory results.

The diphenyl employed melted at 70·5°, and was chemically pure, having been crystallised several times from alcohol. It was converted into the nitro-compound by treatment with concentrated nitric acid in glacial acetic acid solution. By this method 23 grains of pure paranitrodiphenyl, melting at 112—113°, were obtained from 60 grams of diphenyl, a considerable quantity of the ortho-compound being formed at the same time. By reduction with nascent hydrogen, the above quantity of paranitro-compound gave 16 grams of pure paramidodiphenyl, melting at 49°.

Paramidodiphenylsulphonic Acid, $C_{12}H_8(NH_2)\cdot SO_3H$ (probably $NH_2\cdot C_6H_4\cdot C_6H_4\cdot SO_3H = 1\cdot4;\ 1\cdot4$).—No sulphonic acid of amidodiphenyl appears to have been previously obtained. To prepare the above sulphonic acid, 1 part of amidodiphenyl (m. p. 49°) was heated with 4 parts of strong sulphuric acid at a temperature of 130° for half an hour. After cooling, the product was poured into cold water, by which the sulphonic acid, being very insoluble, was precipitated; it was then freed from any more soluble modification by thoroughly washing with water. Paramidodiphenylsulphonic acid melts above 300° with blackening and considerable decomposition. It is practically insoluble in cold water, and scarcely soluble at all, even on boiling.

Sodium Paramidodiphenylsulphonate, $C_{12}H_8(NH_2)\cdot SO_3Na + 2H_2O$.—This salt was obtained by boiling the acid with pure sodium carbonate.

After filtering and allowing to cool, the sodium salt crystallised out in colourless needles, about 1 cm. in length, and in general form closely resembling crystals of potassium nitrate, but with a silky lustre when crushed. For a sodium salt, it is but sparingly soluble in water. The crystals, after thoroughly drying between filter-paper, contain 2 mols. H_2O, both of which they lose at 100°. Analysis gave the following results:—

	Calculated, ($C_{12}H_{10}NSO_3Na + 2H_2O$).	Found.
Na	7·49	7·57
S	10·42	10·54
$2H_2O$	11·73	12·98

Barium Paramidodiphenylsulphonate, $[C_{12}H_8(NH_2)\cdot SO_3]_2Ba + 4H_2O$.—This was prepared from the sodium salt by dissolving the latter in water and adding barium chloride, when the barium salt separated in the form of small needle-shaped crystals. These, after thoroughly drying between filter-paper, contain 4 mols. H_2O, all of which they lose at 100°. The barium salt is only very sparingly soluble in water. Analysis gave the following results:—

	Calculated, $C_{24}H_{20}N_2S_2O_6Ba + 4H_2O$.	Found.
Ba................	19·43	18·53
S..................	9·08	8·66
$4H_2O$	10·21	11·40

We were unable to make a more satisfactory analysis of the barium salt from want of material. The sample analysed possibly still contained a small quantity of moisture.

The sulphonic acid described above appears to be the only one formed by the action of sulphuric acid on paramidodiphenyl under the conditions we have stated, for we were unable to detect the presence of a more soluble acid in the aqueous extract.

The dyes referred to below were made from the above paramidodiphenylsulphonic acid by the following general method:—

The sulphonic acid from 2 grams of amidodiphenyl, after admixture with 2 c.c. strong hydrochloric acid and 20 c.c. water, was diazotised by the addition, with frequent stirring, of 1 gram of potassium nitrite dissolved in 3 c.c. of water. To this was added gradually, with continual stirring, a cold alkaline solution of the requisite phenol. The alkaline phenol solution was previously prepared by dissolving 0·6 gram of ordinary phenol, quinol, or resorcinol, or 1 gram of α- or β-naphthol in 5 c.c. water containing 1 gram caustic soda, and then sufficient hydrochloric acid to make the liquid nearly neutral; it was subsequently made strongly alkaline by the addition of $3\frac{1}{2}$ grams of sodium carbonate dissolved in a minimum of water.

The dye, with the exception of that from quinol, which was very soluble, was thus precipitated, and subsequently collected, and washed with cold water.

Sodium phenolparadiazodiphenylsulphonate,

$$HO{\cdot}C_6H_4{\cdot}N : N{\cdot}C_{12}H_8{\cdot}SO_3Na.$$

—This dye-stuff was obtained as above in the form of an amber-coloured precipitate, which is only sparingly soluble in cold water, but readily soluble on warming.

It dyes wool, and especially silk, a brilliant and very beautiful yellow. To raw jute, it imparts an amber shade, but appears to have little or no affinity for bleached jute yarn.

The *barium salt* was prepared by precipitating a very slightly acid solution of the sodium salt with barium chloride. It forms a yellowish-brown precipitate, which is almost insoluble in cold water. On analysis it gave—

	Calculated, $(C_{18}H_{13}N_2SO_4)_2Ba$.	Found.
Ba................	16·18	15·79
S	7·56	7·36

Sodium resorcinolparadiazodiphenylsulphonate,

$$(HO)_2C_6H_3{\cdot}N : N{\cdot}C_{12}H_8{\cdot}SO_3Na,$$

is a deep brick-red crystalline precipitate, which becomes yellowish-brown on drying. It is only sparingly soluble in cold, but readily soluble in hot water. It dyes silk, wool, and raw jute a beautiful orange, and bleached jute yarn a pink shade, the last fibre, however, appears to have but little affinity for the dye.

The *barium salt*, obtained like that of the preceding compound, is a dark-brown insoluble precipitate. On analysis it gave—

	Calculated, $(C_{18}H_{13}N_2SO_5)_2Ba$.	Found.
Ba................	15·61	15·78
S	7·29	7·35

Sodium Quinolparadiazodiphenylsulphonate,

$$(HO)_2C_6H_3{\cdot}N : N{\cdot}C_{12}H_8{\cdot}SO_3Na.$$

—This compound is very soluble even in cold water, and was not precipitated therefrom by the addition of salt, so that the dye was not obtained in the solid state. Its solution in water is amber-coloured, and dyes silk and raw jute a very pretty golden-amber. On wool, the shade is very much duller, whilst bleached jute yarn does not take up the dye at all.

The *barium salt* is also very soluble in water.

Sodium α-Naphtholparadiazodiphenylsulphonate,

$$HO{\cdot}C_{10}H_6{\cdot}N : N{\cdot}C_{12}H_8{\cdot}SO_3Na,$$

is a deep reddish-brown almost black precipitate, which is fairly soluble in water even when cold. It dyes silk, wool, and raw jute a deep reddish-brown. It has scarcely any affinity, however, for bleached jute.

The *barium salt* is a dark-brown precipitate, which becomes black on drying. It is somewhat soluble in water, much more so in fact than that of the corresponding compound from β-naphthol. On analysis, it gave—

	Calculated. $(C_{22}H_{15}O_4SN_2)_2Ba$.	Found.
Ba................	14·53	14·49
S	6·79	6·77

Sodium β-naphtholparadiazodiphenylsulphonate,

$$HO{\cdot}C_{10}H_6{\cdot}N : N{\cdot}C_{12}H_8{\cdot}SO_3Na.$$

is a bright red precipitate of the colour of red sealing-wax. It is but sparingly soluble in cold, but readily soluble in hot water. It dyes silk, wool, and raw jute a very brilliant red, and bleached jute yarn a reddish-pink shade. It also dyes cotton, mordanted with tin salt or with tannic acid, a bright red; the colour, however, is not fast upon cotton, but is in great part removed by boiling water.

The *barium salt* is a dull red and almost insoluble precipitate, which on analysis gave—

	Calculated. $(C_{22}H_{15}O_4SN_2)_2Ba$.	Found.
Ba...........	14·53	13·96
S	6·79	6·52

When the dye-stuff last described is produced in a liquor, which is only made strongly alkaline with sodium carbonate *after* the mixture of the naphthol with the diazodiphenylsulphonic acid, it is obtained of a much darker and less brilliant red, and is very much more soluble in water. In this form, it dyes silk a dark-red, and wool and raw jute a brownish-red shade. An analysis of the barium salt gave results corresponding with the formula $(HO{\cdot}C_{10}H_6{\cdot}N : N{\cdot}C_{12}H_8.SO_3)_2Ba$.

All the above dyes are fast colours on wool and silk, and are not affected either by boiling water alone, or by boiling water containing half a per cent. of soap, except the yellow dye from phenol, which becomes slightly paler after boiling with soap. In the case of the reddish-brown dye from α-naphthol, the colour, though not weakened by treatment with a boiling soap solution, becomes a purer brown, the red shade being removed.

XXXIX.—*The Combustion of Cyanogen.*

By Harold Dixon, M.A., The Duke of Bedford's Lecturer in Chemistry, Balliol College, Oxford.

A few years ago, on discovering that a dried mixture of carbonic oxide and oxygen would not explode on the passage of an electric spark through it, I made a few experiments on other dried gases, to ascertain whether they showed the same peculiarity. While I found that hydrogen and other gases containing hydrogen, even after long contact with anhydrous phosphoric acid, always exploded with oxygen under the influence of the spark, experiments made with dry cyanogen gave results which inclined me to the belief that cyanogen, like carbonic oxide, did not explode with oxygen when pure, but was oxidised indirectly through the interaction of the small quantity of aqueous vapour usually mixed with it. My experiments were of two kinds. In the first place, a well-dried mixture of cyanogen and air was introduced into the eudiometer of a gas analyser. The pressure being reduced to 100 mm., a spark from a Ruhmkorff coil was passed through the mixture without causing an explosion. The pressure was then raised 5 mm. at a time, and a spark was passed after each increase of pressure. In this way, the pressure was increased to 800 mm. without the spark causing an explosion in the mixture. The tube was then moistened, and the experiment repeated. The spark caused no explosion at pressures less than 300 mm.; at 305 mm. pressure, the gases exploded with violence. In this experiment, the cyanogen seemed to behave in a manner similar to that of carbonic oxide, which when nearly dry is not exploded by a spark at low pressures, but explodes when the pressure is raised. One striking difference, however, was observed between the two cases. When the pressure was gradually increased until the spark caused the explosion of the carbonic oxide and oxygen, the inflammation was noiseless and extremely slow, the blue disc of flame taking some seconds to travel down the eudiometer; but when the cyanogen and oxygen were exploded under 305 mm. pressure, the inflammation appeared instantaneous, and was accompanied by the bright flash, and the "ping" on the mercury characteristic of violent explosions in eudiometers. In the second place, two mixtures of cyanogen and oxygen were kept standing over mercury in contact with anhydrous phosphoric acid for several days in bent eudiometers. On testing these mixtures with sparks from a Holtz machine, I found that neither of them exploded. Tested with the discharge from a coil, one mixture exploded violently, the other was unaffected. I regarded these pre-

liminary experiments as affording *primâ facie* evidence of the non-inflammability of pure cyanogen in oxygen. Other work kept me from examining the reaction more in detail at the time.

On returning to the subject last autumn, I discovered that the explosion of cyanogen and oxygen is independent of the presence or absence of steam. *The explosion depends solely on the nature of the spark.* A strong spark causes the mixture to explode violently, whether wet or dry; a weak spark may be passed through the mixture wet or dry, without apparent effect. Although these experiments form part of a more general investigation (not yet completed) of the phenomena of gaseous explosions, I am glad to take an opportunity of correcting before the Chemical Society, the error to which I formerly leaned.

The cyanogen employed in the following experiments was prepared from mercuric cyanide, powdered and dried at 120°. The dry powder was placed in a piece of combustion tubing, closed at one end, and drawn out into a delivery tube at the other. The gas was collected over dry mercury, and kept in contact with anhydrous phosphoric acid. The oxygen was prepared in a similar manner from powdered potassic chlorate. Mixtures of the dry cyanogen and oxygen were made in short straight eudiometers, furnished with platinum wires fixed at different distances apart. In one tube the wires approached to within about 0·25 mm., in a second to within 0·5 mm.; in the others the distance between the wires varied from 1 mm. to 3 mm. These eudiometers were filled while hot with hot mercury; after the gases had been introduced, short sticks of phosphoric acid were passed up through the mercury into the mixtures. The tubes were then allowed to stand for a fortnight before testing. On passing sparks from a Holtz machine through the mixtures none of them exploded. The smallest spark (0·25 mm.) from the Holtz machine exploded mixtures of hydrogen and oxygen and carbonic oxide and oxygen (damp) under the same conditions. On passing the discharge from a Ruhmkorff coil, no explosion occurred in those tubes in which the platinum wires were close together—from 0·25 to 1 mm. apart; the mixtures in the other tubes exploded violently. Comparative experiments were then made with the gases moist. Sparks from the Holtz machine were passed through all the tubes without explosion; the Ruhmkorff discharge failed to explode the mixture in the three tubes in which the platinum wires were close together, but it caused a violent explosion in the other tubes.*

* Two of these tubes filled with the same mixture were exhibited before the Society on March 18th. Sparks from a Ruhmkorff coil were passed between wires 1 mm. apart in one tube without causing explosion. In the second tube the wires were 3 mm. apart. The first spark passed between them caused a violent explosion.

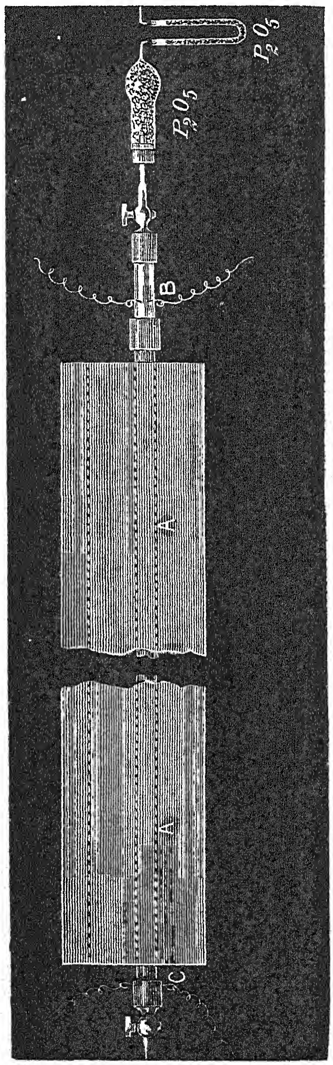
Since the conditions of temperature and pressure were, as nearly as possible, similar in the two series of experiments, it seemed probable that the explosion or non-explosion of cyanogen and oxygen was determined by the nature of the spark, and not by the presence or absence of moisture.

To make sure that a thoroughly dried mixture of cyanogen and oxygen would explode with a powerful spark, I kept the gases in contact with a considerable quantity of anhydrous phosphoric acid for eight weeks. The tube was occasionally shaken, to break up the loosely packed sticks of oxide, and so offer fresh drying surfaces to the gas. On passing a large spark through the gases after the two months' drying, the mixture exploded with the usual violence. In another experiment, the cyanogen was kept ten days in contact with a stick of potash, and was then mixed with dry oxygen in a eudiometer. After the mixture had stood several days in contact with anhydrous phosphoric acid, it exploded violently on the passage of a strong spark. This experiment showed that the explosion of cyanogen was not dependent on the presence of a small quantity of hydrocyanic acid or other substance absorbable by potash.

But it may still be objected that the drying by phosphoric acid, however prolonged, is not really complete, and that the trace of aqueous vapour remaining is sufficient to bring about the explosion, once the reaction is started by a sufficiently strong spark. Supposing, it may be urged, we possessed in chemistry no more powerful drying agent than potash, we should find that a mixture of carbonic oxide and oxygen, dried as thoroughly as our means permitted, would withstand without explosion a spark from a Holtz machine, but would explode when submitted to the discharge of a Ruhmkorff coil. What happens in the case of carbonic oxide dried by potash may happen also in the case of cyanogen dried by phosphoric acid, and no positive evidence has been adduced to show that pure cyanogen and oxygen are capable of exploding, but only that these gases still explode in the presence of an exceedingly minute trace of water. The argument would be unanswerable if it had not been shown that the rate of combination of carbonic oxide and oxygen increases rapidly with the addition of aqueous vapour, whereas the rate of combination of cyanogen and oxygen is not increased, but slightly diminished, by the addition of aqueous vapour to the very dry gases. Exact measurements of the initial velocity of explosion of dry and wet mixtures of cyanogen and oxygen leave little room for doubt that the addition of aqueous vapour only impedes the reaction between the two gases.

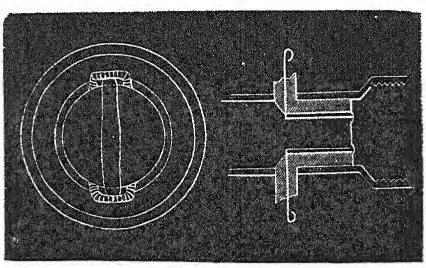
The explosion-rate of cyanogen and oxygen was determined by means of the pendulum chronograph employed in my previous experiments on carbonic oxide and oxygen. The explosion tube was similar

in general design to the one used in the earlier research, but the taps and joints of the new tube were made of hard steel instead of gun-metal, which was found worn away where it had been continually subjected to the molecular bombardment of the heated gases. The explosion-tube AA was 10 feet long. Near one end of it, B, two insulated platinum wires were let into the tube, so that a distance of about



Arrangement of Explosion Tube.

3 mm. separated their points. These wires were connected up with the secondary coil of a large Ruhmkorff. Near the other extremity of the tube, C, were fitted two insulated silver pieces, one on each side of the tube, each connected with a platinum wire passing through a vulcanite block to the outside of the tube. Before each experiment, a narrow strip of silver foil was soldered on to the insulated silver pieces, forming a slender "bridge" across the tube. This silver bridge carried a current from one Grove cell to an electro-magnet, which, so long as the current passed, held down a style against the pull of a light spring; when the explosion, passing down the tube, smashed the silver bridge, the electro-magnet was unmade, and the style, released, sprang upwards at the moment the circuit was broken. A heavy pendulum, carrying a smoked glass plate, passed in its swing in front of the style, which left its trace on the blackened surface. The moment at which the circuit was broken was thus recorded on the plate. At the bottom point of its swing the pendulum broke another circuit connected with the primary coil of the Ruhmkorff. At the moment this primary circuit was broken the induced current in the secondary coil caused a spark to pass between the platinum wires in the explosion-tube, firing the mixtures of gases. The exact moment of firing was thus known. While the explosion was passing along the tube between the firing point and the silver bridge, the style continued to trace an arc of a circle on the moving plate, until, on the explosion reaching the bridge, the circuit was broken, and the style was released from the electro-magnet. The distance travelled by the pendulum between the passage of the spark and the rupture of the bridge—translated into time by means of a standard tuning fork—gave the mean velocity of explosion of the gaseous mixture. One considerable error had to be corrected, the retardation of the electro-magnet, which varied with the strength of the current. This was eliminated by means of a preliminary experiment, made immediately before the explosion. The electro-magnet (detached from the silver bridge) was connected up so that its circuit was broken by the pendu-



Plan of the cap C. Section of the cap C.

lum instead of the primary circuit of the Ruhmkorff. This moment was recorded by the style with the error due to retardation. Without altering the position of the electro-magnet and style, the wires were readjusted and the explosion made. The second mark made by the style gave the moment at which the silver bridge was broken, with the error due to retardation; and since the previous mark gave the moment at which the mixture was fired, also with the error due to retardation, the distance between the two marks gave the duration of the explosion independently of the error, which affected equally the position of both marks.

The gases were collected and measured in a dry iron cylinder over mercury in an annular iron tank. The cyanogen was passed directly from a glass retort through a **U**-tube filled with potash into the holder, previously charged with dry oxygen. The volume of the mixture amounted to half a cubic foot, so that all the experiments could be made with the one mixture. The gases, after mixing, were slowly forced into the dry explosion-tube through two vessels packed with asbestos coated with anhydrous phosphoric acid. Two determinations of the rate of explosion were made with the gases dried in this manner. In a third experiment, the gases were passed into the dry explosion-tube through a **U**-tube packed with fragments of potash; in two other experiments, the gases were made to bubble through water at 15° before entering the tube. The temperature of the room was 15°, and the barometer stood at 763 mm. In the following table, the result of these experiments is given, and for the purpose of comparison a table of the similar experiments with carbonic oxide and oxygen is placed beside it. It must be borne in mind that the rates here given are not the constant rates of the explosive waves of carbonic oxide and of cyanogen. The experiments with carbonic oxide were made in a tube about 3 feet long, of which one-third only was traversed at the full speed of the "explosive wave." In the cyanogen experiments, probably only the first foot was traversed with a constantly increasing velocity, and the remaining 9 feet at full speed.

Mean Initial Rate of Explosion.

1. Carbonic oxide and oxygen.		2. Cyanogen and Oxygen.	
Hygrometric state.	Rate. Meters per sec.	Hygrometric state.	Rate. Meters per sec.
Dried by P_2O_5	36	Dried by P_2O_5.........	813
,, H_2SO_4	119	,, ,, ...	811
Saturated at 10° C.	175	,, KOH	808
,, 35 ,, ...	244	Saturated at 15° C.	752
,, 60 ,, ...	317	,, ,, ...	741

I would call special attention to the *rapid increase* in the explosion-rate of carbonic oxide and oxygen as a trace of water is added to the nearly dry mixture, compared with the *almost inappreciable fall* in velocity as a trace of water is added to the nearly dry mixture of cyanogen and oxygen. Unless we are prepared to admit that the immeasurably small quantity of steam remaining in the gas after passing through the phosphoric acid is enough, or more than enough, to effect the combination of the cyanogen and oxygen *at their maximum rate*, these results seem conclusive that the explosion of cyanogen and oxygen is not brought about by the interaction of a trace of steam, but by a direct action between the gases under the conditions of the experiment.

In a paper (this Journal, Trans., 1885, p. 575) read before the Society last year, I described the action of a heated coil of platinum wire on a dry mixture of carbonic oxide and oxygen. When the coil was raised to redness in the thoroughly dried mixture, the wire glowed intensely for a minute or more, and after cooling the whole of the carbonic oxide was found to be oxidised. No trace of flame was visible in the tube during the combination. A similar experiment made with cyanogen and oxygen gave a curiously analogous result. The tubes employed were the same as those described in my former paper.

When the coil of platinum wire was raised to dull redness by the current, and the circuit was broken, the coil quickly cooled. But when the coil was raised to full redness, it glowed brightly, and continued glowing for half a minute after the circuit was broken. No trace of flame could be detected round the wires. On cooling, the tube was found filled with orange vapour.

The experiment was repeated with the same result, both when the cyanogen and oxygen had been thoroughly dried by long contact with phosphoric acid and when the gases were moist. In the latter case, the orange fumes disappeared in about an hour, and a white crystalline deposit appeared on the mercury. The formation of orange vapour was observed even when the oxygen was taken in considerable defect, but the amount formed was less in this case than when the oxygen was in the normal proportion. On analysing the residual gases left after the coil had been heated in a dry mixture of cyanogen and oxygen, it was found that the combination was not quite complete. Of the cyanogen acted on, about three-fourths had been converted into carbonic acid and one-fourth into carbonic oxide.

This slow combustion of cyanogen in presence of heated platinum was first observed by Davy. In the *Phil. Trans.* of 1817 (p. 80), he says:—

"The chemical changes in general produced by slow combustion

appear worthy of investigation. A wire of platinum introduced under the usual circumstances [heated to low redness] into a mixture of prussic gas and oxygene in excess became ignited to whiteness, and the yellow vapours of nitrous acid were observed in the mixture."

My observations entirely confirm those of Davy. No explosion is produced by the heated wire even when the gases are mixed in the theoretical proportions, and the reaction is independent of the dryness or dampness of the mixture.

The non-explosion of cyanogen and oxygen under the influence of a small spark would appear at first sight to be due to an insufficient temperature being reached. Berthelot (*Compt. rend.*, **95**, 955) has shown that when cyanogen is passed through a tube heated to bright redness, it slowly undergoes decomposition, whereas a strong stream of sparks rapidly splits it up into carbon and nitrogen; and again V. Meyer and Goldschmidt (*Ber.*, 1882, 1161) have shown that while the density of cyanogen remains normal between 100° and 800°, decomposition occurs at 1200°. It would seem therefore plausible to suppose that the *compound* cyanogen is not acted on by the oxygen, but that when broken up by the spark the liberated carbon is oxidised, and the heat so generated breaks up more cyanogen, and so on. It is, however, hard to reconcile with this view the fact that white-hot platinum, though causing a rapid combination of cyanogen and oxygen, yet produces no explosion in the mixture; and again, when a stream of small sparks is passed for several hours through a mixture of cyanogen and oxygen, *partial combination* occurs, and the mixture of gases becomes yellow. The temperature of the small spark is therefore sufficient to produce *some* action between the cyanogen and the oxygen. I hope to make further experiments with a view to decide this question.

XL.—*The Eurhodines, a New Class of Colouring Matters.*

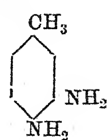
By OTTO N. WITT, Ph.D.

ONE of the methods which lead to the synthesis of dyestuffs consists in the joint oxidation or rather dehydrogenisation of mixtures of various amines, or of amines with phenols; several classes of new colouring matters may thus be obtained according to the amines employed. Thus, the oxidation of a paradiamine with one molecule of a monamine leads to the formation of a member of the indamine-group, whilst one molecule of paradiamine with two molecules of a mon-

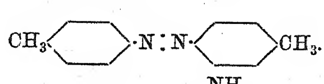
amine yield a safranine, if subjected to the action of powerful oxidisers. Again, a mixture of a paradiamine and a metadiamine in molecular proportions yields on oxidation a compound belonging to the toluylene-blue-group, and if still more hydrogen be removed, a condensation into a derivative of the toluylene-red group is the result. Mixtures of paradiamines and phenols, if oxidised in alkaline or neutral solution, give rise to dyestuffs of the indophenol class, whilst more powerful oxidation in acid solutions results in the formation of substances similar to those discovered and described by R. Meldola. All the classes of dyestuffs enumerated have been studied more or less completely in some of their most important representatives, and we even know the exact chemical constitution of some of them.

Now, in all these reactions, one of the ingredients is always a paradiamine. No attempt has been made to replace this by other substances capable of similar reactions. The reason for this is probably the fact that most of these reactions have not been discovered in the form here given to them. As a rule, certain colour-reactions were obtained with amido-azo- or nitroso-compounds, and it was only recognised on subsequent examination, that the diamine formed by the reduction of these azo- or nitroso-derivatives must be considered as the first cause of the colour-reaction itself. Now as all amido-azo-compounds and nitrosamines known up to a few years ago belonged to the para-series of benzene-derivatives, the constant recurrence of paradiamines in these reactions was very natural.

In 1882, however, the first orthamido-azo-compound was discovered by Nölting and Witt (*Ber.*, **17**, 77), who obtained it by heating pure diazoparamidotoluene with paratoluidine hydrochloride in paratoluidine solution on the water-bath. This substance crystallises in needles (from acetone) or leaflets (from benzene) of a brillant orange colour, and melts at 118·5°; on reduction, it splits up into paratoluidine and orthotoluylenediamine of the m. p. 88·5°, the constitution of which is known to be—

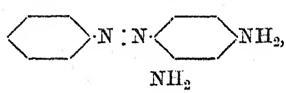


The new amido-azo-compound is therefore, of necessity,



If this substance is treated with hydrochloric acid in alcoholic solution, it yields a hydrochloride which, unlike the salts of paramido-azo-

derivatives dissolves with a green coloration. In the solid state, it forms needles of pale straw colour. If this salt is acted on by primary monamines, such for instance as aniline, it produces, like the salt of a paramido-azo-compound, a dye of the induline-group; now it has been shown by Thomas and Witt (Trans., 1883, 112), that in the induline reaction the amido-azo-compound employed plays no other part than that of dehydrogenising the primary monamine acted upon, and if new proof were needed for the correctness of that view, it would be found in the very fact that an orthamido-azo-compound, acting on aniline, produces the same final result as that obtained with paramido-azo-compounds. But on the other hand, this experiment shows that no reply can be obtained in so simple a manner to the question whether the orthodiamine (formed by the reduction of the orthamido-azo-compound) is capable of forming dyes like its para-isomeride. An unexpected answer to that question was, however, afforded when α-naphthylamine was substituted for aniline in the above experiment; a new dyestuff was obtained, which was so perfectly unlike any colouring matter hitherto observed, that it could at once be recognised as belonging to a new class of compounds, the parent-substance of which could only be the orthotoluylenediamine. This hypothesis was confirmed when other orthamido-azo-compounds were treated with α-naphthylamine hydrochloride. In all cases colouring matters were formed closely resembling the one first obtained. It then became interesting to know how chrysoidine would behave under similar circumstances. This well-known dyestuff is, as may be seen from its constitutional formula—



both a para- and an ortho-amido-azo-compound. If its hydrochloride is heated with α-naphthylamine at 130°, a dyestuff belonging to the new class, and showing all its peculiarities, is obtained; it can, therefore, no longer be doubted that the ortho-position of the amido- and the azo-group is the sole cause of the new reaction, which was carefully investigated. The results obtained I have now the pleasure of laying before the Society.

Action of α-Naphthylamine on Orthamido-azotoluene.

If 22·5 grams (1 mol.) of orthamido-azotoluene (m. p. 118·5°) is mixed with 17·9 grams (1 mol.) of α-naphthylamine hydrochloride, and 50 grams of phenol added, a thick solution of dark emerald-green colour is obtained. The phenol acts merely as a convenient

solvent, and may be replaced by α-naphthylamine, which is, however, not so easily got rid of afterwards. The green coloration is the result of the formation of the hydrochloride of the azo-compound, the salt of the α-naphthylamine yielding up part of its acid to the azo-compound. If this mixture be placed on the water-bath, the green coloration will gradually disappear and be replaced by an intense and brillant scarlet colour. The reaction is then finished and the new dyestuff may be isolated from the mixture. Two different methods may serve equally well this purpose. The first consists in adding to the warm mixture a sufficient quantity of toluene to precipitate all that is insoluble in that solvent. A bright scarlet precipitate, consisting of the hydrochloride of the new dyestuff, is the result. This is collected on a filter, washed with ether, and then introduced into boiling water, acidulated with hydrochloric acid, and dissolved by prolonged boiling. The filtered liquid on cooling deposits long interlaced needles of the pure hydrochloride, which may be collected, washed with very dilute hydrochloric acid, and dried.

Another method of working up the crude melt consists in adding sufficient caustic soda solution to dissolve all the phenol and collecting the yellow precipitate which separates. By treating it with dilute hydrochloric acid, it is transformed into hydrochloride, which may then be treated as before.

If the pure hydrochloride obtained by either of these methods is decomposed by boiling weak ammonia solution, the free base separates as an amorphous precipitate of brilliant yellow colour, which becomes distinctly crystalline on prolonged boiling. It is collected, dried, and recrystallised either from aniline or from phenol, with addition of alcohol. By this means, it is obtained in dark orange glistening needles, which on analysis were found to have the composition $C_{17}H_{13}N_2$.

	Calculated for $C_{17}H_{13}N_3$.	Found. I.	II.	III.
C........	78·8	78·53	78·7	—
H	5·0	—	6·4	—
N	16·2	—	—	15·8

To this substance I have given the name of eurhodine, from εὐ and ρωδός, to recall the red colour of its salts and the eminent crystallising power of the free base.

In order to establish with greater certainty the molecular weight of eurhodine, its hydrochloride was subjected to analysis. This salt was prepared in a state of absolute purity, and in the shape of long, soft, brilliant garnet-coloured needles, by adding dilute hydrochloric acid to a solution of the pure base in acetic acid, filtering, washing with

dilute hydrochloric acid, and drying in a vacuum over quicklime and sulphuric acid. It contains 1 mol. H_2O, which cannot be driven out by heating without partial decomposition of the salt. The elementary constituents of this salt were determined as well as the quantity of free eurhodine base it contains.*

	Calculated for $C_{17}H_{13}N_3,HCl + H_2O$.	Found. I.	II.	III.	IV.
C	65·07	65·71	—	—	—
H......	5·10	5·15	—	—	—
N......	13·40	—	14 02	—	—
Cl	11·33	—	—	11·20	—
$C_{17}H_{13}N_3$	82·60	—	—	—	82·77

The sulphate, oxalate, and tartrate of eurhodine closely resemble the hydrochloride. The nitrate is absolutely insoluble even in boiling water. The acetate could not be obtained in a dry state, but its existence is proved by the fact that eurhodine dissolves with the scarlet colour of its salts in acetic acid.

Eurhodine and its salts show several most striking reactions. In concentrated sulphuric acid they dissolve with intense red colour. This solution on being carefully diluted with water becomes of an intense green. Further addition of water produces a change to scarlet, and the crystalline normal sulphate separates from the solution. Crystallised eurhodine is almost insoluble both in alcohol and in ether; but if it is precipitated in its amorphous condition by adding ammonia to one of its salts in the cold, and then shaken with ether, it is freely taken up by this solvent. The solution is of a bright yellow colour, and shows an intense green fluorescence, quite as strong as that of fluoresceïn but of a more yellow shade. This solution shows a spectrum similar to that of sodium fluoresceïn. Free eurhodine, as well as all its derivatives, show a remarkable indifference to high temperatures. Unlike all other dyestuffs—which are decomposed by dry distillation—eurhodine is volatilised without decomposition. Its vapour on cooling condenses to a voluminous cloud of microscopic crystals. This sublimate strongly resembles the one obtained from certain anthraquinone-derivatives. A few milligrams of eurhodine may be made to fill a large space in this sublimed condition.

All the salts of eurhodine are partly decomposed by pure water. In the presence of an excess of acid, however, they are quite stable.

Eurhodine is a true dye. On silk it dyes a scarlet shade in an acid

* In my preliminary notice (*Ber.*, **19**, **443**) the calculated data were erroneously given as found, and *vice versâ*. This error was subsequently corrected (*Ber.*, **19**, 592).

bath. Its tartrate mixed with tannin and acetic acid, suitably thickened, and printed on cotton mordanted with Turkey-red oil, steamed and washed, produces a red similar to Turkey-red. But the shades produced both on silk and cotton are changed to yellow on prolonged washing in ordinary calcareous water. The original red may be restored by acids.

The formation of eurhodine may be easily accounted for by assuming that equal molecules of orthotoluylenediamine and α-naphthylamine are condensed by the elimination of 6 atoms of hydrogen, the latter being taken up—as is always the case in such reactions—by the reduction of the azo-group—

$$\begin{array}{ll} C_7H_{10}N_2, & \text{orthotoluylenediamine,} \\ C_{10}H_9N_1, & \alpha\text{-naphthylamine,} \\ \hline C_{17}H_{19}N_3 & \\ -\ H_6 & \\ \hline C_{17}H_{13}N_3, & \text{eurhodine.} \end{array}$$

If this hypothesis be correct, the other half of the amidoazo-compound, paratoluidine, must be found free in the crude melt. This is actually the case; paratoluidine was shown to be present in abundance in the mother-liquors from the preparation of the new dye.

Eurhodine is a substance of such marked properties, and its formation is so simple and sure, that it may be utilised as a test, indicating the relative position of any new amidoazo-compound. It is only necessary to heat a trace of the latter with a few crystals of α-naphthylamine hydrochloride and a drop of liquefied phenol, to add an excess of caustic soda and to shake up with ether. If a yellow solution with bright-green fluorescence be obtained, one may be certain that the amidoazo-compound employed belongs to the ortho-series.

Having established the mode of formation as well as the properties of eurhodine, I made some experiments with a view to determining the constitution of the new dye.

Action of Acetic Anhydride.

If acetic anhydride be poured on to eurhodine crystals contained in a dry flask, solution takes place. But very soon crystals begin to separate, and the whole mixture solidifies to a crystalline cake. The acetyl-derivative thus formed may be collected on a filter and washed with alcohol. It forms fine felted needles of straw-yellow colour, which are split up into acetic acid and the free base by the action of strong mineral acids.

The formation of an acetyl-derivative makes it probable that eurhodine contains a primary amido-group, and this probability became a certainty by the examination of the

Action of Acids on Eurhodine.

If eurhodine or one of its salts is heated with dilute hydrochloric or sulphuric acid in a sealed tube, it undergoes a complete and very remarkable decomposition; 3—4 hours at 180° suffice to make every trace of eurhodine disappear. In its stead, yellow crystals separate from the colourless supernatant liquid. On evaporating the latter to dryness, no organic substance could be detected. The entire residue consisted of ammonium chloride or sulphate. The ammonia could only have been formed by an amido-group being eliminated from eurhodine by the action of the acid.

The crystals formed in the tube consisted of a new substance, which possesses both basic and acid properties. It is consequently the phenol corresponding with the primary amine eurhodine. If this be the case, its composition must be $C_{17}H_{12}N_2O$. Analysis proved this supposition to be correct.

	Calculated for $C_{17}H_{12}N_2O$.	Found. I.	II.	III.
C	78·5	78·6	78·2	—
H	4·6	5·1	4·9	—
N	10·7	—	—	10·5
O	6·2	—	—	—

To this phenol of the eurhodine-group, I have given the name of *eurhodol.*

Eurhodol is very insoluble in all solvents with the exception of aniline and phenol. In the amorphous state it dissolves pretty freely in ether; this solution is of a yellow colour, but it is not fluorescent. If slowly crystallised from aniline or phenol, the crystals are of an indistinct orange colour. If, however, the phenolic solution be cooled rapidly, the crystals will be of a bright yellow shade, whilst the aniline solution, by rapid cooling, yields crystals of a vermilion colour. This phenomenon is due to dichroism of the crystals. They possess both red and yellow planes, which are differently developed according to the solvent used.

Eurhodol may be volatilised almost without decomposition. It forms a yellow sublimate similar to that of eurhodine.

In concentrated sulphuric acid, eurhodol dissolves with a dark red colour; water precipitates the sulphate from this solution in yellow flakes.

Concentrated caustic soda solution dissolves eurhodol with an orange colour, and on cooling, a crystallised sodium salt separates. From the dilute soda solution, free eurhodol may be precipitated by the addition of acetic acid.

It thus became evident that eurhodine is the amine, eurhodol the phenol, of a substance $C_{17}H_{12}N_2$, which I tried to discover by studying the

Action of Nitrites on Eurhodine.

If sodic nitrite be added to an acid solution of eurhodine, reaction takes place, and a diazo-compound is formed, as may be seen from the action of the liquid on sodium β-naphthol. It is impossible, however, owing to the great insolubility of all eurhodine-derivatives, either to finish the reaction or to isolate a diazo-compound from the mixture.

Better results were obtained by the action of alkylic nitrites on alcoholic solutions of eurhodine salts. If the acetate is dissolved in alcohol, ethyl nitrite added, and the mixture boiled for two hours on the water-bath, red crystals separate. This substance, which in all probability is the amidoazo-compound of the hypothetical $C_{17}H_{12}N_2$, has not yet been fully examined. It is feebly basic, and dissolves with dark colour in sulphuric acid; on dilution with water, the colour changes to red, and a sulphate separates in crimson flakes.

In presence of a mineral acid, the reaction takes place somewhat differently. Small quantities of the red substance are formed, but the greater part of the eurhodine is acted on with elimination of nitrogen; the liquid soon becoming yellow. The alcohol is then distilled off, and the residue treated with dilute (15 per cent.) hydrochloric acid, which takes up a new base. On adding an alkali, the base is precipitated, and may be collected and recrystallised from a mixture of glacial acetic acid and alcohol. It is thus obtained in long, glistening needles of bright lemon-yellow colour. On analysis these needles proved, however, not to be the expected base $C_{17}H_{12}N_2$. The data obtained showed that it contained oxygen, and that its composition was $C_{19}H_{16}N_2O$.

	Calculated for $C_{19}H_{16}N_2O$.	Found. I.	Found. II.
C	79·16	78·96	—
H	5·56	5·92	—
N	9·72	—	10·23
O	5·56	—	—

This new substance melts at 175°. It is volatilised almost without decomposition at a high temperature. It is easily soluble, with yellow

colour and a faint green fluorescence, in benzene, ether, and acetic acid, less so in alcohol.

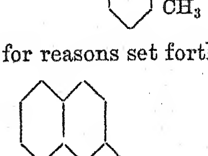
Alcoholic potash, even at 150°, is without any action on the new compound. It is easily soluble in concentrated sulphuric acid, with red colour. It is dissolved by concentrated hydrochlorc acid with an orange coloration, and after a while, brown, bronzy crystals of the hydrochloride separate from the solution. If this solution is heated at 180° in sealed tubes, the compound is transformed into an acid substance resembling eurhodol.

It became evident by these reactions, as well as from the analytical results, that the action of ethyl nitrite had not resulted in the substitution of hydrogen for NH_2, but that, as is sometimes the case, the ethylic ether of the corresponding phenol had been formed, and that the rational formula of the new substance must be written

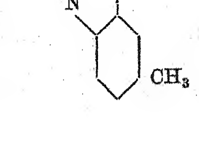
$$C_{17}H_{11}N_2O \cdot C_2H_5.$$

Although thus far my experiments with a view to isolate $C_{17}H_{12}N_2$, the parent-substance of the whole eurhodine-group, had been failures, there was still something to be learned from them respecting the nature of the compound $C_{17}H_{12}N_2$. It will be remembered that phenolic ethers invariably show a strong resemblance to the corresponding hydrocarbons. Thus anisoïl is a compound strongly resembling benzene. In all probability, therefore, the properties of $C_{17}H_{12}N_2$ would be very similar to those of the substance $C_{17}H_{11}N_2O \cdot C_2H_5$.

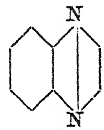
Now, in going over what is known about such substances, we find that a compound, $C_{17}H_{12}N_2$, has already been prepared by Hinsberg (*Ber.*, **18**, 1228), who obtained it by acting on orthotoluylenediamine with β-naphthaquinone, and to which he ascribes the constitutional formula—



which I prefer to write, for reasons set forth hereafter—



This compound, naphthylenetoluquinoxaline, belongs to the class known as quinoxalines, the first and typical representative of which is phenylenequinoxaline—



also prepared by Hinsberg (*Ber.*, **17**, 320) by the action of glyoxal on orthophenylenediamine.

I have prepared Hinsberg's naphthylenetoluquinoxaline, and compared its properties with those of my ether, obtained by the action of ethylic nitrite on eurhodine. The two substances are remarkably similar, and it became thus highly probable that eurhodine is amidonaphthylenetoluquinoxaline.

I was anxious, however, to prove by some other method that the introduction of the amido-group into the molecule of a quinoxaline was sufficient to form a dyestuff of the eurhodine character. I have, therefore, tried to obtain by synthetical means other amidoquinoxalines. My endeavours in that direction were successful.

Phenanthro-eurhodine.

Glyoxal, as may be seen by a glance at its constitutional formula—

$$\begin{array}{l} O:C\cdot H \\ \quad\ | \\ O:C\cdot H \end{array}$$

is the prototype of a long series of compounds which may be described as orthodiketones, and which may be derived from glyoxal by its hydrogen atoms being displaced by other radicals. Thus, by substituting phenyl for hydrogen, we obtain benzil—

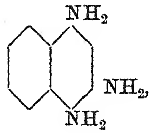
$$\begin{array}{l} O:C\cdot C_6H_5 \\ \quad\ | \\ O:C\cdot C_6H_5 \end{array}.$$

whilst the introduction of the diphenylene-group gives rise to the formation of diphenylene diketone, or phenanthraquinone—

$$\begin{array}{l} O:C—C_6H_4 \\ \quad\ |\quad\ \ | \\ O:C—C_6H_4 \end{array}.$$

Now all these substances, when exposed to the action of orthodiamines, act on the latter like glyoxal, producing substituted quinoxalines. For my purpose, I had, therefore, to react with any or

either of these substances on an amidorthodiamine, or, in other words, on a triamine, two amido-groups of which are in the ortho-position relatively to each other. Such a substance is 1 : 2 : 4-triamido-benzene—

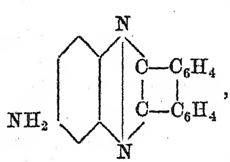


a substance which is formed by the reduction of dinitraniline or chrysoidine. I soon found that it was not necessary for my purposes to isolate this highly unstable substance. It is sufficient to act with any orthodiketone on the crude reduction product of chrysoidine in order to obtain the corresponding eurhodine.

If 2 grams of chrysoidine crystals are dissolved in 50 grams of glacial acetic acid, and an excess of zinc-dust added to this solution, reduction takes place instantaneously, and a colourless liquid is obtained. This is poured off from the zinc-dust (not filtered to avoid the contact of the air), and mixed with the solution of 1 gram of phenanthraquinone in 50 grams of glacial acetic acid. The mixture assumes instantaneously an intense red colour, and the new eurhodine is formed. By adding a large quantity of water, the new compound is precipitated in yellowish-brown flakes, which become bright yellow on prolonged boiling. The precipitate is then collected, and recrystallised from phenol and alcohol. In this way 1·5 grams of small brown crystals are obtained, which on being subjected to analysis proved to have the expected composition $C_{20}H_{13}N_3$.

	Calculated for $C_{20}H_{13}N_3$.	Found. I.	Found. II.
C	81·4	81·4	—
H	4·4	4·7	—
N	14·2	—	14·5

This substance, the constitution of which is undoubtedly—



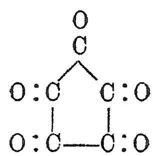
is shown by all its reactions to belong to the eurhodine class of colouring matters.

Its solution in concentrated sulphuric acid is red, and on being

diluted with water becomes yellowish-green, and then again red. Its salts are highly insoluble, and of a carmine-red colour. On adding an alkali to their solution, the free base is precipitated in its amorphous state, and is taken up by ether with yellow colour and the characteristic green fluorescence of the eurhodines. The free base is very insoluble in all solvents, except aniline and phenol. It is volatilised at a high temperature almost without decomposition, and a woolly sublimate is formed in the cooler portions of the tube.

Similar eurhodines were obtained by acting on 1 : 2 : 4-triamidobenzene with any of the orthodiketones capable of forming quinoxalines. The experiment was tried with gyloxal, dioxytartaric (carboxytartronic) acid, benzil, β-naphthaquinone, and isatin. A red dye of the eurhodine character was invariably the result.

The reaction holds good even for polyketones. Thus leuconic acid, which was proved by R. Nietzki to be pentaketopentamethylene—

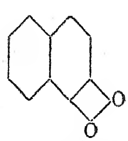


if treated with triamidobenzene, produces a violet colouring matter, which becomes brown on addition of alkalis.

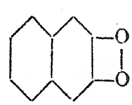
With the results thus obtained, it could no longer be doubted that eurhodine is amidonaphthylenetoluquinoxaline, but there was still one point to elucidate.

Only one naphthylenetoluquinoxaline has hitherto been mentioned, and only one has been prepared by Hinsberg. But, according to our present theoretical views on the constitution of naphthalene, a second isomeride may be predicted. This becomes evident from the following consideration.

Two orthonaphthaquinones are capable of existence, one of which only has hitherto been prepared by Stenhouse and Groves (*Chem. Soc. J.*, 1877, ii, 47; 1878, 415).



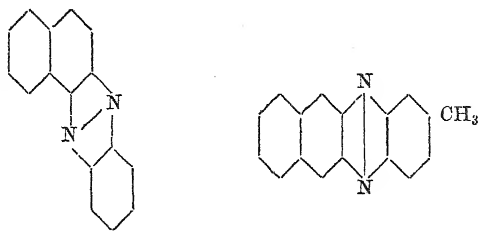
β-Naphthaquinone of Stenhouse and Groves.



Missing isomeride.

Now the second of these, if accessible, would be equally capable of producing a naphthylenetoluquinoxaline if exposed to the action of

orthotoluylenediamine; thus two such bases of the respective formulæ—



may be anticipated, and there is no reason why eurhohine should not be the amido-derivative of the second of these instead of that of the first.

The following experiments which were undertaken with a hope to answer this question have not definitely settled it, but they have resulted in the discovery of the second isomeric quinoxaline and are therefore worthy of being communicated.

Simultaneous Oxidation of α- and β-Naphthol and Orthotoluylenediamine.

If molecular quantities of α-naphthol and orthotoluylenediamine are exposed in an alkaline aqueous solution to the action of potassic ferricyanide, a blue precipitate is obtained, which dissolves in alcohol with a magnificent blue coloration. This dyestuff is very unstable, undergoing spontaneous decomposition in a very short time. As it is, according to all its reactions, a member of the indophenol-group, a description of it is not within the objects of this communication.

Very different results are obtained, however, if β-naphthol be substituted for the α-derivative in this reaction. In this case a dark somewhat tarry precipitate is formed which is collected on a filter and carefully washed with water. It is then treated with dilute (15 per cent.) hydrochloric acid and boiled with it for some time; this treatment is repeated as long as the acid acquires a yellow tint. The dark insoluble substance remaining after this treatment is put aside, whilst the acid extracts are precipitated with caustic soda solution. The grey precipitate thus obtained is collected, washed, dried, and recrystallised from a mixture of glacial acetic acid and alcohol. By this means interlaced needles of a pale straw colour are obtained, which for analysis may be recrystallised from boiling toluene. The substance is thus obtained in the shape of long, well-defined, glistening needles of remarkably definite melting point,

namely, 179·8°, and on analysis gave results agreeing with the formula of a naphthylenetoluquinoxaline, $C_{17}H_{12}N_2$.

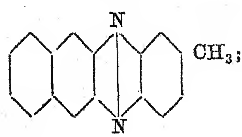
	Calculated for $C_{17}H_{12}N_2$.	Found. I.	Found. II.
C..........	83·61	83·50	—
H..........	4·91	5·34	—
N..........	11·48	—	11·15

This substance is distinctly different from Hinsberg's naphthylenetoluquinoxaline, which melts at 139—142°, and is far more soluble in all the ordinary solvents. Both substances dissolve with an intense red coloration in concentrated sulphuric acid, but the solution of the new substance is of a much more bluish shade. Heated in a dry test tube, the new quinoxaline is volatilised without the slightest decomposition. It dissolves in hydrochloric acid with a bright yellow coloration, and on adding water to this solution, it deposits the hydrochloride in yellow crystals. When treated with fuming sulphuric acid, it is transformed into a sulphonic derivative, whilst concentrated nitric acid gives rise to the formation of a well-defined nitroderivative.

In the production of this base, other oxidising agents may be substituted for potassic ferricyanide. The substance is formed equally well with hydric peroxide, chloride of lime, or freshly prepared plumbic or manganic peroxide. Its formation may be explained by the equation—

$$C_7H_{10}N_2 + C_{10}H_8O + O_2 = C_{17}H_{12}N_2 + 3H_2O.$$

As only two naphthylenetoluquinoxalines are possible, my new compound must have the constitution—

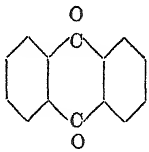


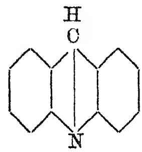
it is a derivative of the missing $\beta\beta$ naphthaquinone, and as may casually be remarked, the first $\beta\beta$-derivative of naphthalene ever prepared.

Before concluding I have to explain my reasons for adopting formulæ for the quinoxalines different from those given to them by Hinsberg.

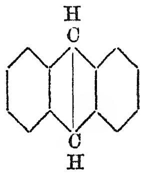
Throughout the experiments connected with this research, I could not help being constantly reminded of two well-known substances, viz., anthraquinone and acridine. Between these two there exists a

definite relationship expressed by the rational formulæ now universally adopted for them.



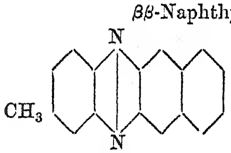


This relationship becomes still more evident if the anthracene formula be added as a connecting link.

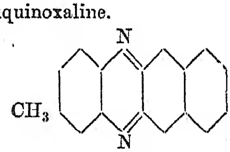


Now if my formula for the quinoxalines be adopted, the similarity of these to anthraquinone and acridine becomes a matter of course, whilst it remains a mystery if Hinsberg's formulæ be adhered to.

$\beta\beta$-Naphthylenetoluquinoxaline.



My formula.



Hinsberg's formula.

Moveover, with Hinsberg's formulæ great difficulties arise if an attempt be made to fill in the double connections of the benzene nuclei. And, notwithstanding all that has been said against them, we have the less reason to treat them lightly, since Fittig's elegant synthesis of α-naphthol from phenylparaconic acid has actually demonstrated their presence. Finally, I may plead in favour of my formulæ that all the other reactions of the quinoxalines, as well as their mode of formation from fatty diketones, may quite as well be accounted for by using my formulæ instead of those of Hinsberg.

I am engaged in the continuation of my researches on the eurhodine class of dyes, and I hope to be able to lay before the Society, in a subsequent communication, the results of experiments now in progress.

Charlottenburg, near Berlin.

XLI.—*Parabenzylphenol and its Derivatives* (Part III), *and on an Isomeric Benzylphenol.*

By Edward H. Rennie, M.A. (Sydney), D.Sc. (London), Professor of Chemistry in the University of Adelaide, S.A.

In my former papers (Trans., 1882, 33, 220), the benzylphenol discovered by Paterno was shown to belong to the *para*-series of compounds, and many of its derivatives were described. Since those papers were published, want of time and opportunity has prevented me from continuing the work; some results recently obtained, however, are now laid before the Society, in the hope that the investigation, which has again been interrupted, may before long be completed.

In preparing material for the earlier part of this work, an oil was expressed from the crude crystalline parabenzylphenol; this was mixed with the alcoholic mother-liquor from the recrystallisation of the latter, and preserved. An examination of this product has led to some interesting results.

The alcohol having been evaporated, the residue was mixed with a suitable proportion of ordinary concentrated sulphuric acid, and heated for some time over the water-bath. When nearly the whole had dissolved, the mixture was diluted with water, neutralised with barium carbonate, well boiled, and filtered. To the filtrate, barium hydrate was added in slight excess, causing a bulky precipitate of the basic barium parabenzylphenolsulphonate. This was collected and washed, and the filtrate reserved for examination.

Further Examination of Dinitroparabenzylphenol.—The precipitate just described having been converted in the ordinary way into the potassium salt, the latter was purified by recrystallisation, and used as a source of the dinitro-derivative already described (Trans., 1882, 222, 226), in order to examine this substance more closely.

The potassium salt was first converted into the nitrosulphonate by the method already given, the latter suspended in slightly diluted nitric acid (through which a current of air had been passed for some time), and the whole warmed on the water-bath with stirring, until an oily liquid began to separate. During this operation, a strong smell of benzaldehyde was noticed. The oil, which solidified on cooling, was collected, and purified by several recrystallisations. It was identical in appearance with that formerly prepared, but the melting point was 85—86°, a little lower than that previously observed (87—88°). Some of this substance was converted into the

potassium salt, and the latter recrystallised. It proved to be anhydrous, and gave the following result on analysis :—

0·1118 gram substance gave 0·0315 gram K_2SO_4 = 0·0142 gram K = 12 63 per cent.

Theory for $C_6H_5{\cdot}CH_2{\cdot}C_6H_2(NO_2)_2{\cdot}OK$ = 12·50 per cent.

On adding a solution of the potassium salt to a solution of barium chloride, a dense yellow precipitate was formed. This is sparingly soluble in boiling water, and crystallises therefrom in yellow anhydrous prisms. On analysis—

0·2545 gram substance yielded 0·086 gram $BaSO_4$ = 0·05056 gram Ba = 19·86 per cent.

Theory for $\begin{matrix} C_6H_5{\cdot}CH_2{\cdot}C_6H_2(NO_2)_2O \\ C_6H_5{\cdot}CH_2{\cdot}C_6H_2(NO_2)_2O \end{matrix}{>}Ba$ = 20·06 per cent.

On warming the dinitro-derivative gently with concentrated nitric acid, it was converted, as in previous experiments, into the trinitro-derivative; but on boiling with slightly diluted nitric acid, red fumes came off, a strong smell of benzaldehyde was noticed, and the substance entirely disappeared, no precipitate being formed on the addition of water. On evaporating repeatedly with water to get rid of the excess of nitric acid, and cooling, a pale yellow substance crystallised out; this after two or three crystallisations from water melted at 121—122°. When boiled with potassic carbonate and cooled, it yielded the characteristic needles of potassium trinitrophenol. On analysis—

0·1623 substance gave 0·053 gram K_2SO_4 = 0·2375 gram K = 1·462 per cent.

Theory for $C_6H_2(NO_2)_3OK$ = 14·60 per cent.

This decomposition, before unnoticed, takes place easily, and explains the small yield of the dinitro-derivative referred to in a previous paper: in fact, as above mentioned, there was a strong smell of benzaldehyde noticeable in the preparation of this derivative (doubtless from the oxidation of the benzyl-group), and the liquid when filtered, evaporated, and boiled with potassic carbonate, yielded a large crop of crystals of potassium trinitrophenol. Crystals obtained in this way gave the following results on analysis :—

0·508 gram substance gave 0·168 gram K_2SO_4 = 0·07531 gram K = 14·82 per cent.

Theory 14·60 per cent.

The formation of trinitrophenol in this way (precisely analogous to the formation of ortho-brom-α-dinitrophenol [$C_6H_2(OH)NO_2NO_2Br$ =

1 : 2 : 4 : 6] from nitro-bromobenzylphenol) shows clearly that in dinitrobenzylphenol the nitro-groups occupy the two ortho-positions.

Examination of the Filtrate after Precipitation of the Basic Barium Parabenzylphenolsulphonate.—The filtrate after removal of the basic barium salt was evaporated to the consistency of a syrup, but as it did not promise to crystallise well, potassium carbonate was added in slight excess, the barium carbonate filtered off, and the filtrate evaporated. On standing, it became a mass of crystals. These were dried by the filter-pump, and recrystallised until colourless. Prepared in this way, the salt forms a mass of fine white needles. The following are the results of analysis :—

0·641 gram air-dried substance lost 0·0855 gram at 100° = 13·34 per cent.

0·475 gram air-dried substance lost 0·0625 gram at 100° = 13·15 per cent.

Theory for $C_6H_5{\cdot}CH_2{\cdot}C_6H_3(OH){\cdot}SO_3K + 2\frac{1}{2}H_2O$ = 12·97 per cent.

0·5555 gram anhydrous salt gave 0·161 gram K_2SO_4 = 0·722 gram K = 12·99 per cent.

Theory for $C_6H_5{\cdot}CH_2{\cdot}C_6H_3(OH)SO_3K$ = 12·91 per cent.

The salt, therefore, is a potassium benzylphenolsulphonate, but it differs from the corresponding salt of parabenzylphenol entirely in appearance, and in containing $2\frac{1}{2}$ mols. H_2O; it must be derived, therefore, either from an *ortho-* or a *meta-*benzylphenol.

Action of Nitric Acid on the new Sulphonate.—On mixing this salt with dilute nitric acid (1 : 1), it is easily converted into a nitrosulphonate, sparingly soluble in water and alcohol, and crystallising from the latter in pale-yellow shining anhydrous scales, which in a thin layer resemble gold leaf. On analysis—

0·351 gram substance gave 0·0875 gram K_2SO_4 = 0·0392 gram K = 11·17 per cent.

Theory for $C_6H_5{\cdot}CH_2{\cdot}C_6H_2{\cdot}NO_2{\cdot}OH{\cdot}SO_3K$ = 11·24 per cent.

On warming this nitrosulphonate on the water-bath with slightly diluted nitric acid, an oily substance soon separated, which solidified to a crystalline mass on cooling. After repeated crystallisations from alcohol, it formed pale yellow rosettes, melting at 81—82°. It is much paler in colour than dinitroparabenzylphenol. On analysis, it yielded the following result:—

0·208 gram substance yielded 19·6 c.c. nitrogen at 28°, and 756 mm. = 0·17 c.c. at 0°, and 760 mm. = 0·022125 gram = 10 63 per cent.

Theory requires 10·22 per cent.

It was converted into the potassium salt in the usual way and yielded pale orange needles, totally different in colour from the corresponding compound derived from parabenzylphenol. After recrystallisation, the following results were obtained on analysis :—

Three determinations of water of crystallisation gave 5·45, 5·66, and 5·40 per cent. respectively, 1 mol. H_2O requiring 5·45 per cent.

Two determinations of potassium gave 12·35 and 12·32 per cent. respectively. Theory requiring 12·50 per cent.

With barium chloride, a solution of the potassium salt gives a bulky yellow precipitate, sparingly soluble in boiling water, and crystallising therefrom in dark yellow needles. On analysis—

0·466 gram substance (air-dried) lost 0·012 gram at 100° = 2·57 per cent.

Theory for 1 mol. H_2O requires 2·56 per cent., leaving 0·454 gram anhydrous salt, which yielded—

0·1504 gram $BaSO_4$ = 0·08843 gram Ba = 19·5 per cent.
Theory = 20·06 per cent.

In the anhydrous condition, this salt is deep red, but on exposure to the air it speedily absorbs water, and regains its original colour and weight. The substance from which these salts are derived is evidently a dinitrobenzylphenol, but it differs widely from its isomeride previously described.

During its preparation, a slight smell of benzaldehyde is developed, but on boiling the pure substance for some time with slightly diluted nitric acid, no appreciable quantity of trinitrophenol is produced. Other decomposition products seem to be formed, the nature of which remains undetermined for the present. When treated with a mixture of concentrated nitric and sulphuric acids, it slowly dissolves; and on adding water a substance is precipitated, which can be obtained by crystallisation from alcohol, in pale lemon-yellow needles. It is but sparingly soluble in cold alcohol, and yields a yellow potassium salt; it is probably a higher nitro-derivative, but at present material is wanting to decide the question.

Action of Bromine on the new Sulphonate.—Six grams of the potassium salt were dissolved in water, and about 3·5 grams of bromine dropped in slowly, with constant agitation. The mixture became slightly warm, and deposited white flocks of a substance which melted to an oily liquid on heating to boiling. As the liquor cooled, the oil solidified to a mass of crystals, leaving the supernatant fluid clear. The experiment was repeated with the addition of ice, but it was not found possible to prevent the formation of the white crystalline substance. The latter is easily soluble in alcohol, ether, acetic

acid, and solution of the caustic alkalis, but is practically insoluble in water. It crystallises from a mixture of alcohol and water in a mass of minute silky needles, which melt about 91°. It is probably a dibromo-derivative, but at present material is wanted for further examination. When warmed with potassium dichromate and sulphuric acid, it yields a yellowish substance, probably a quinone; this awaits further investigation.

The clear aqueous liquid from which the substance just described had separated, yielded a crop of crystals on evaporation. After recrystallisation, these form small anhydrous prisms, having the peculiar white glistening appearance of the phenolbromosulphonates. On analysis they gave the following results:—

0·442 gram substance gave 0·100 gram K_2SO_4 = 0·04482 K = 10·14 per cent.

Theory for $C_6H_5{\cdot}CH_2{\cdot}C_6H_2(OH)Br{\cdot}SO_3K$ = 10·23 per cent.

An attempt was made to prepare a nitrobromo-derivative by the action of nitric acid on this salt, but apparently bromine was given off and a nitrosulphonate formed.

Action of Bromine on the new Nitrosulphonate.—When a solution of the potassium nitrosulphonate is shaken with the requisite quantity of bromine (slowly added), the latter slowly disappears, and a yellowish substance separates, which can be obtained in straw-coloured scales by crystallisation from alcohol. The specimen thus prepared began to show signs of melting at 105°, but did not become quite liquid until 109—110°. It was small in quantity, and, perhaps, was not thoroughly purified. A bromine determination gave the following results:—

0·1095 gram substance gave 0·066 gram AgBr = 0·02808 gram Br = 26·51 per cent.

Theory requires 25·97 per cent.

On boiling with potassic carbonate, it yielded a red potassium-derivative, which did not crystallise easily, being rather soluble in water. The quantity was so small that it could not be thoroughly purified; the numbers obtained on analysis, however, leave little doubt that the substance is a nitro-bromo-benzylphenol isomeric with that previously described. One specimen of the potassium salt yielded 10·62 per cent. of potassium instead of 11·27 per cent. as required by theory.

All the compounds described in the latter part of this paper differ so widely from the derivatives of parabenzylphenol, that there can be no doubt that they are derived either from ortho- or from metabenzylphenol, probably the former; at present, however, there is no evidence

in favour of one or the other. I hope shortly to obtain more material and continue this investigation with a view of examining these new compounds more closely; also to ascertain if possible whether the higher portions of the distillate from which the crude benzylphenol is separated contains any dibenzylphenol, a substance yet unknown.

XLII.—*On Water of Crystallisation.*

By SPENCER UMFREVILLE PICKERING, M.A., Professor of Chemistry at Bedford College.

THE nature of water of crystallisation, and the relation which it bears to the salt with which it is associated, has always been, and still remains, one of the problems least understood in the domain of chemistry. The energy with which it is held by many salts, the thermal phenomena attending its combination, and the marked changes which its presence induces in the appearance and physical characteristics of a salt, would lead us to rank these hydrates amongst true chemical compounds: on the other hand, the fact that it may generally be removed without involving further decomposition of the molecule, that it does not, in the few cases where investigation has been possible, alter the chemical reactions of the salt, and further, that its presence can rarely if ever be expressed according to our ordinary ideas of atomic valency, must ever differentiate hydrated salts from "atomic" compounds, although that difference may be one of degree only and not of kind.*

This difference would appear to have given rise to various unwarrantable assumptions as to the nature of these compounds, and to have led in some cases to the ignoring altogether the possibility of their being subject to many of the laws which, with atomic compounds, are of fundamental importance.

Till the true nature of hydrates be established this possibility must

* In a paper read before this Society (*Abst. of Proc.*, 1885, 122, and pamphlet), I suggested that these "molecular" or "residual" compounds owed their existence to the valencies of the atoms not being representable by whole numbers, thus in any molecule a certain amount of unsaturated or residual valency would exist capable of exerting itself on another molecule, and thereby combining with it to form a so-called molecular compound. Such compounds, therefore, may still be regarded as being composed of integral molecules, although their existence will be due to no new "molecular attraction," but to the known attraction of *atoms* only.

never be overlooked, and except on the strongest evidence no arguments must be admitted but such as would hold good if applied to atomic compounds.

In the present communication, the validity of two very important conclusions which have been drawn respecting water of crystallisation, and which would appear to be universally accepted, will be discussed. These conclusions are:—

(1.) That the various molecules of water in a hydrated salt are not always similar in every respect, but that they differ from each other in their heat of combination, their specific volume, and in other points; that, in fact, a hydrated salt is not always, as regards its water, a symmetrical substance.

(2.) That in some cases one or more of these water molecules is of a totally different nature to the others, being water of constitution and not water of crystallisation at all.

The term "water of constitution" or of "halhydration" was originally applied by Graham (*Trans. Roy. Soc. Edin.*, **13**, 297; *Chem. Soc. Mem.*, **1**, 82, 106; *Phil. Mag.*, **6**, **10**, **11**) to one of the molecules of water in the sulphates of the magnesian metals: unfortunately, however, it is a misnomer, and as such it has created a misconception of the views which it represents (see p. 429).

The gist of this theory is that the so-called constitutional water is not *water* at all, but hydrogen and oxygen forming part of the salt nucleus itself; crystallised magnesium sulphate is not the heptahydrate of $SO_2(MgO_2)$ but the hexhydrate of $SO(MgO_2)(HO)_2$, that this latter salt (improperly regarded as a monohydrate, $SO_2(MgO_2)H_2O$) is an "atomic" compound decomposable by heat into $SO_2(MgO_2)$ + H_2O, just as monosodium phosphate, $PO(NaO)(HO)_2$, is decomposed by the same agent into a totally different salt, $PO_2(NaO)$ and H_2O.

This theory has been further extended towards a second water molecule in the sulphates, and is generally expressed in terms which admit of no misconstruction, thus*:—$SO_2(OH)_2,H_2O$ "may be regarded as a tetrabasic acid of the formula $SO(OH)_4$. . . . Salts of this tetrabasic acid are known. . . . A third hydrate, $SO_2(OH)_2,2H_2O$, corresponding to a hexabasic acid, $S(OH)_6$, was obtained. . . . Salts of this hexabasic acid are also known. . . . Sulphuric acid forms several classes of salts, of which the following compounds may be taken as typical examples:—Tetrabasic zincic sulphate, $SO(ZnO_2)_2$†; hexabasic zincic sulphate, $S(ZnO_2)_3$; crystallised gypsum, $S(CaO_2)(HO)_4$; gypsum dried at 100°, $SO(CaO_2)(HO)_2$; gypsum dried at 200°, $SO_2(CaO_2)$."

* Frankland and Japp (*Inorg. Chem.*, 292—295).

† Graphic formulæ being given in the text quoted.

A. *General Considerations.*

It will be seen at the outset that the representation of the water present in some salts as being "constitutional," increases rather than decreases our difficulties in explaining so-called water of crystallisation, for a vast number of salts contain a much larger proportion of water than can possibly be represented as constitutional, and we are consequently forced to class them in a different category from others, which according to their properties and reactions should be precisely similar compounds.

The constitutional water theory would seem to borrow an air of probability from a study of the so-called organic acids. The water with which these are united is in no case *greater* than that which would be necessary to form the "ortho-" acid, and the existence of perfectly definite ethereal salts corresponding to these acids, and of similar substances derived from the aldehydes, renders it most probable that these hydrated acids are in reality "ortho-" acids or acid hydrols and not mere hydrates. But it must be remembered at the same time that if such is their constitution they are not real acids at all but *alcohols*, and that though they may form "ethereal salts" with organic radicles, we should not, therefore, expect them necessarily to form true salts with the metals. Nor do they appear to do so. A study of the better known salts, the formates, acetates, carbonates, and oxalates for instance, shows that the proportion of water in the hydrated salts, or of metallic oxide in the basic salts, is continually in excess of that which it is possible to represent as atomically combined, and that no greater number of instances exist where the proportion would permit of the salt being regarded as a derivative of the ortho-acid, than where the proportion would not do so. There are a few cases* where it is usual to regard a salt as a derivative of the "ortho-" acid, but whether they are such is merely a matter of speculation unsupported by any evidence whatever.

With inorganic acids, the case would appear to be different. These acids do not affect the "ortho" form more readily than their salts do. There is but one instance, $Sb(OH)_5$, where an ortho-acid is known without having salts corresponding to it; and again, some of the acids form compounds with water, which must undoubtedly be regarded as

* Such as the acid formates, $H{\cdot}COONa, H{\cdot}COOH, H_2O$ being considered as $HC(ONa)(OH){\cdot}O{\cdot}CH(OH)_2$, although the water present in them is a very variable quantity and far below the amount required by the formula (Bineau, *Annalen* [3], **19**, 291; **21**, 183); also malachite, Cu_2CO_4,H_2O, and azurite, $Cu_3H_2(CO_4)_2$; $CaCO_4,H_2O$, and one or two others, though it is difficult to believe that these basic salts are totally different in their constitution from the other basic carbonates of copper, cadmium, cobalt, lead, nickel, and zinc, which contain too large a proportion of the metal to admit of such a method of representation.

hydrates merely, such as $2H_3AsO_4,H_2O$ and $H_2SO_3,8H_2O$, both known in the solid condition, while Berthelot's researches on the heat produced by dilution,* have shown that in the dissolved state hydrates exist corresponding approximately to the formulæ $HNO_3,2H_2O$; $HNO_3,15H_2O$; $HCl,6{\cdot}5H_2O$; $HBr,4{\cdot}5H_2O$; and $HI,4{\cdot}5H_2O$.

It cannot, of course, for a moment be doubted that many metallic salts do exist containing hydrogen and oxygen as part of the salt molecule. It will, therefore, be necessary to examine the reasons which have led to the conclusion in such cases, in order to ascertain whether similar reasons hold good in other cases under dispute, and especially in the case of the sulphates.

These reasons may be summed up as follows:—

(1.) The existence of a large number of reactions which are most consistently represented by regarding the salt as containing a certain radicle such as NO_2 in the nitrates, PO in the phosphates, &c. These reactions certainly point to SO_2 and not S being the radicle in the sulphates, the acid acting as a dibasic, and not as a tetrabasic or hexabasic one.

(2.) The salt cannot be regarded as containing water unless its formula is doubled, whereas its formation and reactions are opposed to such a course. The phosphites afford an instance in point. This argument, however, cannot be applied to the sulphates.

(3.) Where the hydrogen in a salt is displaceable by a metal, as it is in the supposed orthosulphuric acid, we find that—

(*a.*) If in considerable quantity, the salt is strongly acid.
(*b.*) A metal may be substituted for it atom by atom.
(*c.*) A large number of salts exist in which the whole of it is displaced by a metal.

(*a.*) Now, if a hydrated sulphate be a derivative of orthosulphuric acid, it will contain no less than four atoms of acid hydrogen; the presence of *some* acid hydrogen, it is true, does not necessarily produce an acid reaction, but it is reasonable to expect that a compound with such a large amount of it would be strongly acid, instead of being, as it is in every case where partial dissociation has not occurred, absolutely neutral. The phosphates, NaH_2PO_4, with a much smaller proportion of acid hydrogen, are strongly acid.

* *Annalen* [5], **4**, 446; *Compt. rend.*, **86**, 279. Berthelot discusses the conclusions drawn by Roscoe and Dittmar (*Chem. Soc. J.*, **12**, 128; **13**, 156) on the composition of the acids when boiling under various pressures, and shows that they are consistent with the idea that the solutions boiling at 760 mm. consist of definite hough not very stable hydrates (*Méc. Chem.*, **1**, 517; **2**, 149).

(*b*.) The second feature is a more important one. In no case with which we are acquainted, except that of metastannic acid,* do we find the acid hydrogen displaced only in stages of two atoms at a time, the acid salts contain either an even or uneven number of hydrogen-atoms indifferently. With sulphuric acid itself, this is the case as regards two of the hydrogen-atoms, we get $NaHSO_4$ as well as Na_2SO_4, but if this same acid is to be regarded as containing six such hydrogen-atoms, then the remaining four are certainly different from the first two, for (regarding basic salts for a moment as true salts) when displaced at all, they are always displaced in pairs. Surely this must show that they are present in pairs, as in H_2O, and not as separate independent atoms.

(*c*.) The third point is still more important. Instead of there existing a large number of metallic orthosulphates, there are none. Basic salts, I maintain, cannot be regarded as neutral salts. The method of their formation and their characteristics are entirely opposed to such a view; but, besides this, we have two very powerful arguments against such a supposition: (1) The very metals which displace acid hydrogen most energetically—the alkali metals—are the very ones which form no basic salts, and, generally speaking, the greater the energy with which a metal displaces this hydrogen, and the more stable the salt is which it thereby forms, the less tendency does it show to form a basic salt. (2) By far the greater number of the basic salts contain too large a proportion of oxygen to be represented as ortho-salts. So many of those which are said to exist are indefinite mixtures, that I will mention those only which I have had occasion to investigate myself, the sulphates of copper, iron, and aluminium (Trans., 1880, 807; *Chem. News*, **45**, 121, 133, 146; **47**, 181). The only definite compounds were found to be $CuSO_4,2CuO$, $CuSO_4,3CuO$, $Fe_2(SO_4)_3,5H_2O$.† Only the first of these contains a proportion of metallic oxide which would permit of its being considered as an ortho-salt (and even here the water with which it is combined would indicate that the formula should be doubled, see *Chem. News*, **52**, 2), and it is scarcely rational to consider it as an atomic compound, while the other similar basic copper salt and the basic iron salt, both of which are more definite and more stable than the former, must perforce be regarded as mere molecular compounds. That a basic salt is in every respect analogous to a hydrated salt is the most rational view to take of its constitution, but such a view is possible only when the water in the hydrated salt is regarded as such, and not as hydrogen and oxygen.

A study of the basic salts which an acid forms is, I believe, one of

* Possibly also the polymetaborates, but this is by no means certain.

† Three compounds only where thirty were said to exist.

the most valuable means of ascertaining the nature of the acid. Many of the reasons which would lead us to deny the existence of orthosulphuric acid might be urged with equal force against that of orthoboric acid, but the manner in which the neutral orthoborates are obtained, and the character of the metals contained in them, shows at once that they are true salts (see Bloxam, *Chem. Soc. J.*, **12**, 177; **14**, 143).

(4.) When a true acid ortho-salt is heated so as to be decomposed with evolution of water, the residue, the meta- or pyro-salt, exhibits characteristic reactions which show it to be a different compound from the ortho-salt. This can only be verified in cases where the distinction between the salts is further characterised by the lower ones (meta or pyro) not combining with water except under special conditions, or after the lapse of an appreciable, often a very long, time. The phosphates, antimonates, and stannates form instances in point; with the arsenates and borates, however, mere contact with water is sufficient to convert them into the ortho-salts, and, therefore, no special force can be given to the argument that the sulphates yield identical solutions whatever the state of hydration in which the salt may have been before its dissolution.

Only one other plea might be urged for the existence of orthosulphates if it appeared that the majority, or even some noticeable proportion of hydrated salts contained $2H_2O$, or of basic salts, $2M''O$. The answer to this is singularly clear. Of all the hydrates ordinarily met with, there are fewer with two molecules of water than with any other number; in fact, but one dihydrate* is known, $CaSO_4,2H_2O$, and even here a considerable weight of evidence derived from various sources proves that the molecule is more complicated, and that it should be doubled, the water being removable in fourths. Basic sulphates with $2M''O$ are scarcely more numerous than dihydrates. Those of Cu, Di, G, Hg, and Y† have been described, but what weight should be attached to the statements as to their existence may be judged from what has already been said respecting basic salts.

It is not possible, even in the case of sulphuric acid itself, to argue

* By partial dehydration and special methods, dihydrated sulphates such as those of Cd, Cu, Mg, Zn, Co, Mn, and Fe may be prepared, but they cannot be described as salts in a normal state of hydration, and indeed doubts must in many cases be entertained as to the definiteness of their nature.

† The introduction of $ZnSO_4,2ZnO$ in the passage quoted on p. 412 as an instance of an orthosulphate, is even less happy than that of gypsum. I have failed to find any mention whatever of such a compound. It may also be remarked that not the slightest indication of the hydrate $CaSO_4,H_2O$ has ever been obtained; the salt dried at 100—120° has the composition represented by $2CaSO_4,H_2O$.

that the compounds which it forms with water are not mere hydrates There is a considerable development of heat when the highest isolated compound, $H_2SO_4,2H_2O$, is dissolved in water, indicating, no doubt, the existence of still higher hydrates, and there is no sudden break which would suggest that these are different in nature from the lower ones; they might all, even including SO_3,H_2O itself, well be members of the same series;* the numbers are approximately—

$$\begin{aligned} SO_3 + H_2O &= 21{,}320 \text{ cal.} \\ H_2SO_4 + H_2O &= 6{,}379 \text{ ,,} \\ H_2SO_4,H_2O + H_2O &= 3{,}039 \text{ ,,} \\ H_2SO_4,2H_2O + H_2O &= 1{,}719 \text{ ,,} \\ H_2SO_4,3H_2O + H_2O &= 1{,}183 \text{ ,,} \\ H_2SO_4,4H_2O + H_2O &= 750 \text{ ,,} \\ H_2SO_4,5H_2O + H_2O &= 550 \text{ ,,} \end{aligned}$$

Enough will have been said to render any further discussion as to the existence of two constitutional water molecules in the sulphates superfluous. All the arguments brought forward against these two molecules apply with equal force against the existence of only one, but in opposition to these arguments we find various reasons given in favour of there being one such molecule present. These reasons may be included under the title of—

B. *Experimental Evidence.*

Three considerations appear to have conduced originally to the theory of there being one "constitutional water" molecule in the magnesian sulphates. These were—

(1.) That considerably more heat is developed in the combination of one molecule of water with the anhydrous salt than in the subsequent addition of any other single molecule.

(2.) That one of the molecules of water present is retained at a much higher temperature than any of the others.

(3.) That one only of them can be displaced by a molecule of sulphate of potassium or some allied metal, forming a double salt such as $MgSO_4,K_2SO_4,6H_2O$.

Heat of Hydration.

The general conclusions deduced from experiments on the heat of hydration of salts is that, in most cases, the various water molecules in a hydrated salt bear different relations to the salt nucleus. It will be found, however, that these deductions rest on a most unwarrantable

* The same equation will represent all the results, within the limit of experimental error (Thomsen, *Thermochem.*, 3, 57).

assumption, namely, that the relation which the water molecules bear towards each other and towards the salt nucleus is absolutely unalterable by any process short of their removal.

We are indebted to Thomsen (*J. pr. Chem.*, 18, 5) for the most complete series of investigations on this subject. It is true that I have already (Trans., 1885, 102) had occasion to show that Thomsen's data were incorrect, since the substances with which he dealt were not definite hydrates but mixtures of different hydrates; but even if this had been otherwise he would, no doubt, have obtained results of the same general character, and would have drawn the same general conclusions from them.

Thomsen attempted to ascertain the heat of combination of the individual molecules of water in certain hydrated salts by determining the different heats of dissolution of the same salt hydrated to various extents. The difference in the heats of dissolution of any two hydrates, such as $MgSO_4,3H_2O$ and $MgSO_4,4H_2O$, gave the thermal value of the reaction [$MgSO_4,3H_2O + H_2O$]. Now this, he assumes, gives the heat of combination of the fourth molecule of water in the hydrate $MgSO_4,4H_2O$, but unless the above-mentioned unwarrantable hypothesis be accepted, it does, I maintain, do nothing of the sort. It can tell us the heat of combination of the fourth molecule only in the event of the heat of combination of the other three remaining entirely unaltered by the addition of this fourth molecule, and we have no more reason for making such an assumption in the case of these molecular compounds than we have in the case of atomic compounds, and certainly no one would venture to state that the heat of combination of $Pb + S$, and the relations which exist between these atoms in the compound PbS, remain entirely unaltered by their assumption of 4 atoms of oxygen to form $PbSO_4$. Lead sulphate does not *contain* lead sulphide, no more does a tetrahydrated salt *contain* the trihydrate. The thermal reaction [$MgSO_4,3H_2O + H_2O$] is made up of two distinct quantities—(1) the decomposition of the trihydrate, (2) the formation of the tetrahydrate; and all we can measure is the algebraic difference between the two. The water molecules in the one hydrate may be in a state of combination very different from that in which they exist in another hydrate, and in any one hydrate all the water molecules may or may not be similar; but experiments such as Thomsen's can throw no light whatever on the question.*

* We may push this line of argument still farther, and question, for instance, whether a determination of the heat evolved in the reaction ($MgSO_4 + H_2O$) gives us any information as to the heat of combination of $MgSO_4$ with the H_2O, or whether the relations of the atoms composing the anhydrous salt are not modified by the combination of the salt with another molecule. I have elsewhere (*Chem. Soc. Proc.*, 1885, 122) stated that various experimental evidence favours such a

The heat which is evolved on the addition of one molecule of water to the anhydrous salt is certainly very much greater proportionately than that evolved on the addition of more than one; but even if Thomsen's numbers be accepted, they only show that this difference is one of degree only and not of kind; the first molecule in $MgSO_4,7H_2O$ develops in combining 7980 cal., according to him, and the other six only 17,100 cal. altogether, and yet he proves they may all be members of the same series.* A little consideration, moreover, will show that the facts observed here with hydrated salts are but a counterpart of those shown by atomic compounds. The heat of combination of one atom of oxygen with two of hydrogen is 69,000 cal., but the combination of a second actually *absorbs* 22,400 cal. Who would argue from this difference that in hydrogen dioxide the two atoms of oxygen are united to the hydrogen with different degrees of energy and perform entirely different functions? And yet on the strength of a precisely similar but much smaller difference, it is argued that the molecules of water in a hydrated salt are different not only in degree but also in kind. Such an argument is utterly worthless.

There is one conclusion, however, which may be drawn from Thomsen's work. As with magnesium sulphate, so with the sulphates of zinc, copper, manganese, the double sulphates, and other salts, he found that the diminution in the heat of dissolution was not always directly proportional to the amount of water present in them; whereas with the sulphate,† carbonate, and the two phosphates of sodium it

view, but it is probable that the addition of any fresh molecule to a "molecular" compound (H_2O to $MgSO_4,3H_2O$) would affect the relationship of the various *molecules* ($MgSO_4$ and $3H_2O$) to a far greater extent than it would the relationship of the *atoms* constituting those molecules.

* This relationship is brought out so clearly in the case of magnesium sulphate, that it would almost carry conviction with it, in spite of the hypothesis on which it rests, were it not that Thomsen was certainly dealing with indefinite mixtures, and that his determination of the heat of dissolution of the monohydrate contains an error of about 1100 cal., a quantity which would entirely destroy these fancied relations (*loc. sup. cit.*). It is instructive to compare the results obtained in the case of magnesium sulphate with those obtained in some other cases where the water present cannot be regarded as constitutional, and where, nevertheless, the first molecules appear to be combined with far greater energy than the subsequent ones, thus:—

In $MgSO_4,7H_2O$, heat of combination of the—

1st,	2nd,	3rd,	4th,	5th,	6th,	7th H_2O.
6980	2250	3600	3210	2230	2110	3700

In $SrBr_2,6H_2O$, heat of combination of the—

1st,	2nd,	3rd,	4th,	5th,	6th H_2O.
6150	3800	3100	3100	3160	4000

† His numbers for the heat of dissolution of the anhydrous salt being emended in accordance with the author's observations (Trans., 1884, 689).

was so. Such a proportionality is, no doubt, due to the partially dehydrated specimens being mixtures of the fully hydrated and anhydrous salt in various proportions; where, then, this proportionality does not exist, we may conclude that the partially dehydrated salt contains some intermediate hydrates, which under favourable circumstances might have been isolated, and each of which possesses a special heat of dissolution different from that of a mixture of the same percentage composition.

Temperature of Dehydration.

It is difficult to attach much weight to arguments deduced from any difference in the temperatures at which the various molecules of water are expelled from a hydrated salt, for in some cases (that of the typical magnesium sulphate itself) this difference is very small, not more than 10° C. (Trans., 1885, 101), and if we admit such reasoning here we should have, in order to be consistent, to admit it in all cases, and devise some different principle of combination for every molecule of water which is driven off at a different temperature. But, apart from this consideration, any argument based on such behaviour will be found, as in the case of Thomsen's deductions, to be drawn in opposition to one of the fundamental principles of chemistry: that no chemical action is a single action, but is the result of at least two or three distinct actions. We cannot assert that magnesium sulphate, $MgSO_4,7H_2O$, on being heated *gives up* six molecules of water because they are loosely combined, and *retains* the seventh because it is more energetically combined; all we can state is that the heptahydrate, being incapable of existing in dry air at 155°, is *decomposed*, and the monohydrate, which is capable of existing under such conditions, is *formed*. These two views of the same action are radically different: the second is a mere statement of the facts themselves, whereas the first asserts that a lower hydrate is actually *contained* in a higher one—that the monohydrate is a *residue* from the heptahydrate. What reasons have we for stating this to be so here any more than in other cases of decomposition? Because hydrogen dioxide gives up one of its atoms of oxygen at a temperature many hundred degrees lower than that at which the second one is parted with, no one has ever ventured to suggest that the two oxygen-atoms in hydrogen dioxide are, therefore, different, one being combined very energetically, the other very feebly. An argument which will not hold good in one case must not be blindly accepted in the other. Hydrogen dioxide does not *contain* water, and heptahydrated magnesium sulphate does not *contain* the monohydrate.

Whatever experimental evidence can be brought to bear on the

question certainly tends to show that this is the case; that the further addition of water to a hydrated salt necessitates an alteration in the relations existing between the salt nucleus and the water molecule already combined with it, and that similar intramolecular changes occur in other cases where so-called molecular compounds are considered.

(1.) If a fully hydrated salt really *contained* the lower hydrates, it is difficult to understand why these latter should not be successively formed in the process of dehydration, since the abstraction of one molecule of water would not, *ex hypothesi*, influence the stability of the remaining ones. But, as is well known, it is generally impossible to obtain intermediate hydrates by dehydration, even when these are capable of a separate existence.

(2.) According to Hannay (*Chem. Soc. J.*, 1877, ii, 389), when hydrated zinc sulphate is heated at 100°, it does not fuse, but as soon as three molecules of its water have been driven off, it does so. Now the only probable explanation of a loss of water causing an increase in fusibility must be that the loss is accompanied by some change in the constitution of the salt.

(3.) If partial dehydration consists of the removal of the more weakly combined molecules leaving a *residue* containing the more energetically combined ones, hydration would exhibit the reverse phenomena; the lower hydrates containing the strongly combined molecules would be formed first, and then the higher hydrates. But this is not the case. I have mentioned elsewhere (Trans., 1885, 103) that the peculiarities in the manner in which anhydrous and monohydrated magnesium sulphates dissolve show that the latter is not formed during the hydration of the former; the anhydrous salt cakes but dissolves quickly; the monohydrate does not cake, but takes a considerable time to dissolve, rendering the liquid milky meanwhile. On the view here advocated, no difficulty would be met in explaining this fact; whichever hydrate was the most stable under the given conditions, would be formed directly; none of the water molecules in it being combined with greater energy than the others, none of them would be taken up before the others. What also can be the explanation of the monohydrate taking so much longer to assimilate six molecules of water than the anhydrous salt does to assimilate seven, unless it be that some alteration in the constitution of the salt is necessitated?

(4.) Hannay (Trans., 1879, 456) mentions another instance, which, if verified, would go far to show that the addition of a fresh molecule to a compound molecular group influences the energy with which the original components of this group were held together. He states that the double salt, $[(ZnSO_4,7H_2O)(MgSO_4,7H_2O)]$, when

dried at 100°, loses its water at twice the rate with which the components, $ZnSO_4,7H_2O$ and $MgSO_4,7H_2O$, do, and leaves a residue retaining only $2H_2O$, whereas a mixture of the uncombined molecules would retain double this quantity of water.* We cannot, however, go so far as Hannay does, and say that "the two salts in combining have expended *one-half* of the affinity of the anhydrous salt for its water of crystallisation," unless it can be proved that "affinity is inversely proportional to the rate of loss."

(5.) Some facts which I have recently brought before this Society (Trans., 1886, 260) afford very strong evidence, though not amounting to absolute proof, in favour of the views here advocated. It was ascertained that as the temperature rises, a saline solution experiences changes which would indicate (in most cases) the formation of higher hydrates; it was also proved that the heat of combination of a salt with its water of crystallisation was not a constant quantity; and further, that the temperature at which this latter experienced a diminution was the same at which a higher hydrate began to form in the solution, as if the energy of combination between the salt and its water increased as the temperature rose, till this increase became so considerable that a larger amount of water became attached, but that the increased energy expended on this necessitated a diminution of that expended on the water previously combined. A similar intramolecular compensation was observed in the case of the double salts; those temperatures at which the heat of combination of a salt, such as $CuSO_4,K_2SO_4$, with its water of crystallisation was greatest, corresponded to those at which the heat of combination of the component molecules, $CuSO_4$ and K_2SO_4 in the anhydrous salt, was smallest.

These arguments, meagre though they be, all tend to throw doubt on a theory which at the best is entirely unsupported by experimental evidence, and in my opinion is irrational.

The temperature of 100° does not appear to be critical as regards water of crystallisation. On the one hand there are many instances in which "constitutional" water is evolved at or below 100°, such as orthoboric and the ortho-organic acids; and on the other hand water, which must be regarded as water of crystallisation, is, in very many cases, retained at a much higher temperature; thus many chlorides, $MnCl_2$ for instance, retain a notable quantity of water even at 220°;

* This statement (1879, 459) is unfortunately irreconcilable with those in a previous paper (1877, ii, 388 and 399), "that the dehydration of magnesium sulphate might be pushed till only *one* molecule was left at 100°," and that with zinc sulphate at 100°, "the dehydration becomes very slow till *six* molecules have gone, and there it stops."

so also with many metallic oxides: thus $K_2O,5H_2O$* is stable at temperatures below 400°. Indeed, the temperature at which water of crystallisation is evolved, not only from different salts, but also from different hydrates of the same salt, as well as its rate of evolution, would appear to show the same amount of variation as is observed in the temperature and rate of other chemical decompositions.

Although the lower hydrates of a salt are undoubtedly more stable than the higher ones (just as H_2O is more stable than H_2O_2), the results of dehydration afford no grounds for considering that there is any difference either in kind or in degree, in the manner in which the various water molecules in any particular hydrate are combined, nor can the temperature of 100° be regarded as being more critical with reference to water of crystallisation than 50°, 150°, or any other temperature.†

Double Salts.

The existence of these salts forms the third reason generally assigned for regarding the magnesian sulphates as containing a molecule of constitutional water, sometimes termed in consequence water of halhydration. The view that the double salt, such as

$$MgSO_4,K_2SO_4,6H_2O,$$

is derived from the corresponding magnesian sulphate,

$$MgSO_4,H_2O,6H_2O,$$

by the displacement of a molecule of water in it by potassium sulphate, was controverted by Thomsen, who endeavoured to show that the $6H_2O$ in the one salt is combined with a different heat evolution to the $6H_2O$ in the other salt. Even if it be admitted that Thomsen's work did measure the heat of chemical combination of these water molecules, the fact that it is different in the one salt to what it is in the other is surely not an argument that the one is not a true displacement-product of the other; it would, indeed, be very remarkable if the displacement of the one molecule of water did not affect the

* Maumené (*Bull. Soc. Chim.*, **44**, 578) assigns much more complicated formulæ to this and similar hydrates, $9K_2O,47H_2O$, &c.

† It must be remembered that 100° is a temperature which for convenience sake is generally employed when examining the behaviour of hydrated salts: no investigation has been undertaken, as far as I am aware, to ascertain whether it is preferable to any other temperature.

The rate of dehydration of some substances has been studied by Hannay (*loc. cit.*) and by Ramsay (*Chem. Soc. J.*, 1877, ii, 395). Müller-Erzbach (*Ber.*, **17**, 1417; *Ann. Russ. Chem.* [2], **23**, 607; *Chem. Centr.*, 1885, 470) has examined the vapour-tensions of various hydrated salts. The tensions became inappreciable after the loss of amounts of water which were very various in different and even similar cases, and which did not represent any simple molecular proportions.

other molecules present. I have elsewhere (this vol., p. 13) pointed out that the simple manner in which these double salts are formed from the magnesian sulphates, and the accurate manner in which the various characteristics of these latter are reproduced in the double salt, justify us in regarding these as most evident instances of displacement. The argument based on their existence then is that only one molecule of water in $MgSO_4,7H_2O$ being thus displaceable, this one must be different from the other six. The very fact that one of these water molecules has been displaced may, however, be the very reason why the others are not displaceable. With atomic compounds, we know that displacement of one atom affects the others, rendering their displacement more easy or more difficult, sometimes even impossible; and any argument which is based on the gratuitous assumption that with hydrates no such intramolecular reaction takes place, must be valueless. We might as well argue that three of the hydrogen-atoms in benzene itself were different from the other three, because three only can be displaced by NO_2, as that one of the water molecules in $MgSO_4,7H_2O$ is different from the rest because one only can be displaced by the K_2SO_4.*

Not only can no argument in favour of the constitutional theory be derived from these double salts, but they even afford a strong argument against this theory.

If the double salt is derived from $M''{<}^{O}_{O}{>}SO{<}^{OH}_{OH},6H_2O$, a sulphate with one molecule of "constitutional" water, its constitution will be $M''{<}^{O}_{O}{>}SO{<}^{O}_{O}{>}SO{<}^{OK}_{OK},6H_2O$.

Now I have shown (this vol., p. 1) that the anhydrous copper potassium sulphate and probably all its congeners exist in three distinct modifications, differentiated by their colour, specific heat, and heat of dissolution. The first of these modifications is obtained by the simple dehydration of the hydrated salt at the lowest possible temperature, whereas the other two are produced from this one only at considerably higher temperatures. If, therefore, any of these anhydrous salts contains the constituent sulphates united in the same manner in which they are in the hydrated compound, it is the first or α-modification and not either of the others.

Now in all cases where the specific heat of a hydrated salt has been

* It is not difficult to see the reasons which may render the displacement of more than one molecule improbable. From the numbers obtained, it would seem probable that the displacement of one molecule of water by K_2SO_4, has considerably increased the heat of combination of the other six; but even a small increase in their heat of combination would render it impossible to displace them by K_2SO_4, for such a displacement would be accompanied by a decided *absorption* of heat.

determined, it appears that this specific heat is equal or very nearly equal to the sum of those of the anhydrous salt and the water present (reckoned as solid water), the heat of dissolution also of such a salt indicates that it behaves as if it were a mere mixture of such constituents (this vol., p. 7); of the three modifications of the double salts, there is only one which acts in a similar manner, it is the α-salt only which has a specific heat identical, within experimental error, with that of a mixture of its constituents (p. 14), and which dissolves with the same* heat evolution as would such a mixture; this modification therefore, and consequently the hydrated salt from which it is so simply obtained, is the only one which must be regarded as possessing a constitution similar to that of a true hydrated salt, the potassium sulphate in it behaving in the same way as water of crystallisation in the latter. If, then, it be regarded as being derived from the single sulphate by simple displacement of water, that water must be water of crystallisation and not water of constitution.

Specific Heat.

It has been ascertained, as indicated above, that the specific heat of a hydrated salt is equal to the sum of that of the anhydrous salt and the water reckoned as solid water, and this will be found to hold as good in the case of the monohydrated sulphates as in any other case (see the determinations made by Kopp and by Pape). Much stress, however, cannot be laid on this similarity, for the numbers obtained show great discrepancies, and can be regarded as being but approximations at the best; it would probably require the adoption of far more delicate methods than those at present known, in order to distinguish between water of crystallisation and the elements of water, for while the specific heat of the former is 9°, that of $H_2 + O$ in solid compounds would appear to be 8·6°† (Kopp, *Jahresb.*, 1864, 43).

Volume of Solid Hydrated Salts.

The specific volume of solid hydrated salts would appear to be subject to considerable variations. In the case of certain highly hydrated salts, such as sodium sulphate and phosphate, the volume is

* See p. 288, where a misprint of 600 cal. in the numbers given on p. 7 and 15 is corrected. We may state this fact in another way: the formation of the α-salt from its constituents evolves 29 cal., the β-salt 3249 cal., and the γ-salt 1331 cal., the one in which the heat of formation is least, the α-salt, is that in which the constituents are less energetically united, the β- and γ-modifications both being formed with considerable evolution of heat are the two which, if any, are atomic compounds.

† With reference to the variations in the specific heat of hydrated salts, see this vol., p. 285.

exactly equal to that of the solid water contained in the salt, whereas in other cases the volume is equal to the sum of those of the salt and the solid water present (Playfair and Joule, *Chem. Soc. Mem.*, **2**, 401; **3**, 57, 199; *Chem. Soc. J.*, **1**, 121, 129).

The volumes of the so-called magnesian sulphates in various states of hydration were examined by Thorpe and Watts (Trans., 1880, 102). The general result of this examination was to show that the volumes of the sulphates of this group of metals (Cu, Mn, Fe, Ni, Co, Mg, Zn) were practically identical in whatever state of hydration they were, and that the water molecules in the higher hydrates occupied a larger volume than those in the lower hydrates. The mean results were as follows:—

Volume of the salt with—	0,	1,	2,	3,	4,	5,	6,	7 H_2O.
	44·8	55·5	68·8	83·3	98·7	112·9	130	146·1

from which they conclude—

Vol. of the	1st,	2nd,	3rd,	4th,	5th,	6th,	7th water molecule.
	10·7,	13·3,	14·5,	15·4,	14·2,	17·1,	16·1,

the volume of one molecule of ice at the same temperature being about 19·8. These numbers can only be regarded as approximations, as in many cases it was impossible to obtain the required hydrate, and in others the definiteness of the product was doubtful. However, they were all obtained by definite processes and not by partial dehydration, and therefore no objection to the data can be made on that score, as in the case of Thomsen's experiments on their heat of dissolution. But precisely the same objections can be made to the conclusions drawn by Thorpe and Watts as to those drawn by Thomsen; the two cases are exactly parallel. The fact determined is simply the volumes of xH_2O in the hydrate containing that amount of water; the difference between this and the volume of that with $(x + 1)H_2O$ does not give us the volume of the $(x + 1)$th molecule, unless we assume that the volumes of the x molecules have been entirely unaffected by the addition of another molecule, and this we have no right whatever to assume. We may say that the volumes of the lower hydrates are comparatively less than those of the higher ones, but we cannot say anything whatever about the volumes of the different molecules in any particular hydrate, they may all be equal or all unequal; experiments such as these can throw no light on the question.

The water in the monohydrate would appear to occupy a much smaller volume than any of the others, indicating no doubt its superior stability, but the difference is not such as to warrant any conclusion

that it is different in kind from the others. The difference between it and the second molecule for instance, is 2·6, while a difference greater than this exists between the second and the sixth or seventh, and even between the fifth and sixth, where there can be no doubt about both molecules being water of crystallisation.

Volumes of Salts in Solution.

Enough will have been said already to show that the arguments on which the "constitutional" molecule theory was originally founded are utterly fallacious; there is, however, another argument deduced from the volumes occupied by salts in solution which at first sight would appear to be a strong one.

Nicol (*Phil. Mag.*, 1884, 179) has shown that in a large number of cases the change of volume accompanying the displacement of one radicle by another (whether metal or non-metal) in a salt in solution is a constant quantity, independent of the nature of the other radicle present: thus the substitution of Br for Cl increases the volume of a salt solution ($1 : 100H_2O$) by 7·4, whether the metal with which the halogen is combined be sodium or potassium. He also finds that this holds good whether the salts are hydrated or anhydrous in the solid condition. Now the increase in volume produced by substituting Cl for $\frac{SO_4}{2}$ he finds to be 9·2 in most cases, but that with the magnesian sulphates it is only 6·8, and consequently, he argues, we are not substituting Cl for $\frac{SO_4}{2}$ in these latter, but for something else, namely, for $\frac{SO_4}{2}$ + a molecule of constitutional water. The data, however, from which these conclusions are drawn appear to be very insufficient and capable of other interpretations. They are as follows:—

Metal in the salts examined.	Difference. $Cl - \frac{(SO_4)}{2}$.
K	8·9
Na	9·2
$\frac{Cd}{2}$	8·9
L	9·8
	9·2

Magnesium Sulphates.

$\frac{Cu}{2}$	6·1
$\frac{CO}{2}$	6·4
$\frac{Ni}{2}$	7·8
	6·8

The separation of these metals into two groups would seem to have been effected on somewhat arbitrary principles. According to the class of metal taken, cadmium has certainly a good claim to be ranked with the magnesium sulphates, for although (like copper and manganese sulphate) it does not crystallise with $7H_2O$, it forms double salts with the sulphates of potassium, sodium, and ammonium, isomorphous with the corresponding double salts of copper, cobalt, and nickel. A distinction based on the numbers obtained would seem to be more arbitrary still. The difference between two members of the different groups is as small as 1·1 in the case of L and Ni, whereas individual members of the *same* group show a difference of 0·9 (K and L), and even as much as 1·7 (Cu and Ni).

More concordant results were obtained when the solutions of the various sulphates were precipitated by barium chloride, the expansion which took place in the various cases was as follows:—

Na_2SO_4	43·5
K_2SO_4	43·9
$CuSO_4$	37·7
$ZnSO_4$	37·8
$NiSO_4$	37·2
$MnSO_4$	38·6

the numbers in the last four cases being undoubtedly smaller than in the first two. It may well be questioned, however, whether these data are not much too meagre to found any general conclusions upon; there are so many points of difference between the alkali metals (represented here by only two members) and the magnesian metals, that it seems rash to conclude that these different volume-changes are due to one peculiarity more than to another. Sulphates belonging to other classes of metals should certainly be examined also. However, accepting the data as sufficient, the conclusion drawn is that the volume of a molecule of water of constitution is 24·4, or 6·4 *greater* than that of water of solution or water of crystallisation; but further on, p. 192, Nicol shows, from a comparison of the sodium phosphates, that "the elements of water in a molecule occupy *less* volume than water," the

volume being 9·9 in one case and 13·9 in another, according as they are contained in one molecule of the salt or two. This is entirely irreconcilable with the previous conclusion; the very meaning of the "constitutional molecule" is that it is not water at all, but the *elements of water*, the monohydrated sulphates according to this theory are identical in constitution with the acid phosphates; if then these elements of water occupy a much smaller volume than H_2O, we have a perfect proof that no such "elements" or constitutional water is present in the magnesian sulphates. Even were it thoroughly established that these salts do exhibit anomalies in their volumes, and that these anomalies are due to the water combined with them, this would do no more than show that the different molecules of water of *crystallisation* may bear a different relation towards the same salt.*

On the strength of his conclusions that this "constitutional" water occupies a greater volume than water of crystallisation, whereas the experiments of Thorpe and Watts (see above) on solid hydrated salts would indicate that it should occupy a smaller volume, Nicol concludes that water of crystallisation, or, as we ought to term it, combined water, does not exist in solution at all, *i.e.*, that a salt solution contains the salt in the anhydrous condition.

"At first sight," he proceeds, "the experiments of Thomsen and others, on the heat of hydration of various salts, lend much support to the view that water of crystallisation does exist as such in solution; for there is no doubt that while in very many cases a hydrated salt dissolves in water with absorption of heat, the same salt when dehydrated evolves heat on solution. But is it not possible that the act of solution of a dehydrated salt consists, first, in the taking up of water to form a hydrate; and that this hydrate, in dissolving, parts with its water, which thus becomes indistinguishable from the rest of the water"? The simple answer to this question is that it is *not* possible. Nicol seems to have overlooked the fundamental principle of thermochemistry, a principle which is but a special application of the conservation of energy, that the decomposition of any compound absorbs precisely the same amount of heat as its formation evolves, that if the hydrate be first formed and then decomposed the thermal results will be the same as if it had never been formed at all. That a hydrate is formed, as Nicol admits, when a dehydrated salt is thrown into water is unquestioned, it can be seen, felt, removed, and analysed; that its formation is attended with considerable development of heat is equally sure, the quantity developed can be measured, and is generally a very considerable quantity. Even if we can reconcile ourselves to the

* Whatever conclusions may be drawn from this work, it must be remembered that their bearing on the nature of water in a *solid* salt is but indirect, since they apply directly to the dissolved salt only.

belief that the water which will at one moment combine so energetically with the salt, will the next decompose the very compound which it has formed; even if we believe that this salt with such a strong attraction for water is capable of existing in the presence of water without combining with it, we are driven to admit that the force which causes it to do so is not only more powerful than the *chemical* attraction between the salt and its water, but that in its operation it evolves more heat than the chemical combination. This force Nicol considers to be the resultant of the attraction of (1) salt molecule for salt molecule, (2) water for water, and (3) water for salt; the first two act in opposition to the last; it is therefore only the predominance of this last over the sum of the other two which causes dissolution. It is scarcely necessary to point out that no amount of attraction, chemical or otherwise, can of itself produce the least particle of heat; it is only the actions which result from this attraction which can do so; according to his theory, then, the motion of the drawing together of the salt and water molecules, although it does not draw them into that state of close connection known as chemical combination, must produce a greater amount of heat than does their actual combination itself. Surely this is quite inadmissible.

Nicol's views on the nature of solution are based chiefly on the fact that the volume of water of crystallisation in the liquid state is indistinguishable from that of ordinary water. But why should we attach more weight to such a fact with liquid salts than we do with solid salts? We might as well argue that in a solid hydrated salt the water is not combined with the salt because it possesses a specific heat (and specific volume too, in many cases) indistinguishable from that of solid water.

Very many more thermal phenomena besides the one above discussed are inexplicable except on the hypothesis that hydrates do exist in solution; whether their existence can give us a full explanation of all the facts about dissolution or not, is quite another question, and one which it would be foreign to the subject of the present paper to discuss.*

Conclusion.

The results of the present examination may be summarised as follows:—

1. The theory that the sulphates contain either one or two molecules

* For this reason, also, I refrain from discussing the results obtained by various physicists on the alteration of the freezing point, temperature of maximum density, and tension of water by the addition of salts thereto—no conclusions adverse to the opinions expressed in the present communication are, I believe, deducible from these results.

of "constitutional" water finds no confirmation whatever in general considerations as to their formation, properties, composition, and analogies with other salts.

2. The most decisive evidence as to whether a given salt is an "ortho-" salt or a basic salt is afforded by the nature of the metals which form such salts, and by ascertaining whether it displaces the hydrogen-atoms singly or in pairs. Those metals which displace "acid" hydrogen most energetically are the ones which exhibit least tendency to form basic salts.

3. Although the heat of hydration of a salt indicates that the lower hydrates are generally more stable than the higher ones, it gives no information whatever as to whether the various water molecules in any particular hydrate are all similarly combined or not.

4. Nor is any information on this point afforded by the different temperatures at which the water molecules are evolved.

5. Experimental evidence, no less than general considerations, show that the water molecules in a lower hydrate are affected by the addition of more water. The higher hydrate does not *contain* the lower one.

6. The displacement of one of the water molecules in the magnesian sulphates by K_2SO_4, affords no grounds for the supposition that the one displaced differed in any respect from the others. The physical properties of the resulting double salt afford a strong argument in favour of the displaced molecule being water of crystallisation only.

7. The specific heats of hydrated salts throw no light on the nature of the different water molecules.

8. Experiments with the solid hydrated sulphates of the magnesian metals show that the volume of the water in the lower hydrates is relatively less than that in the higher hydrates. But the difference is not such as would indicate any difference in nature of any of the various hydrates, and certainly affords no information as to the volumes of the individual water molecules in any particular hydrate.

9. The volume of dissolved salts may show that one molecule of water in these magnesian sulphates differs from the rest; but the data available are at present too meagre to warrant any definite conclusions being drawn. At any rate, whatever the difference may be, it is of exactly the opposite nature to that which would be exhibited if it were water of "constitution."

10. With the exception of this last-mentioned fact, which can at present be regarded as a possibility only, we have no grounds for supposing that the various water molecules in a hydrated salt are not all combined in a similar manner, and do not all occupy exactly the same position with regard to the salt nucleus; that, in short, a hydrated salt is not a symmetrical substance. At the same time, it must be

admitted that we have no positive evidence to show that it is symmetrical, and we must, therefore, regard it as such provisionally only, till some unquestionable evidence in favour of or against this view be forthcoming.

XLIII.—*On an Acetic Ferment which forms Cellulose.*

By Adrian J. Brown.

During my work on the chemical actions of *Bacterium aceti*, described in a previous paper (this vol., p. 172), I met with the peculiar acetic ferment commonly known as the "*vinegar plant*" or "*mother*." This ferment differed so much in appearance from any form of *B. aceti* I had noticed, that it seemed probable it was a distinct organism. In order to ascertain this, and also to enable me to study its chemical actions, I obtained pure cultivations by a combination of the fractional and dilution methods in the way I described in my previous paper. The nutrient solutions used for this purpose were composed of red wine diluted with half its bulk of water, and rendered acid with 1 per cent. of acetic acid in the form of ordinary vinegar. This liquid strongly favours the growth of the acetic ferments, and is at the same time very prejudicial to the growth of most other organisms.*

In order to be more certain of the purity of the culture, inoculations of it were made in gelatin and beerwort. In about ten days, well-defined colonies of the ferment commenced to grow in this solid nutrient mixture. Many of these colonies were transferred separately to suitable sterilised liquids, and in every case the characteristic growth of the "vinegar plant" appeared. There can be no doubt, therefore, that the cultures thus obtained were quite pure.

A pure cultivation of the "vinegar plant," when commencing to grow in a liquid favourable to its free development, is usually first noticed as a jelly-like translucent mass on the surface of the culture fluid; this growth rapidly increases until the whole surface of the liquid is covered with a gelatinous membrane, which, under very favourable circumstances, may attain a thickness of 25 mm. This membrane is slightly heavier than water, and when gently agitated

* In all experiments mentioned in this paper, the same methods were used, and the same precautions taken, with regard to the sterilising of culture fluids, cottonwool, &c., as have been previously described by me (this vol., p. 173).

sinks until its upper surface is covered with liquid, when another layer of the ferment at once commences to grow above the old one. Frequently as many as five or six layers of growth are thus formed, causing the whole mass to appear striated when observed laterally. In colour, the membrane is white and translucent, unless grown in coloured solutions, in which case it assumes somewhat the colour of the liquid.

On removing the membrane from the liquid, it is found to be very tough, especially if an attempt is made to tear it across its plane of growth; parallel to this plane, however, it is much more easily divided into a number of layers, evidently representing successive stages of growth. In touch and general appearance, the "vinegar plant" has a remarkable resemblance to a soft animal membrane.

If the "vinegar plant" is grown in a liquid unfavourable to its free growth, such as yeast-water, it is first observed as a jelly-like, very transparent mass at the bottom of the solution; and this gradually increases in size until the surface is reached, and the liquid appears to be almost entirely filled with it. Close examination of this mass, however, shows that it is composed of extremely attenuated membranes of the ferment, which ramify through the bulk of the liquid, and actually enclose much of it, thus giving the jelly-like appearance.

When the ferment is grown in solid gelatin and malt-wort, spherical colonies are formed, but these appear only on the surface or a short distance from it. The colonies that grow on the surface gradually spread out into a film, resembling the ordinary membrane which grows on nutrient liquids. Gelatin is not liquefied by the ferment.

The membranous growth of the "vinegar plant" is the only form of growth which I have succeeded in developing. During my work with pure growths, I have made successfully more than 100 cultivations in solutions often varying very much in their chemical composition; but however much the character of the nutrient fluids, or other conditions of growth, were altered, the ferment always reproduced itself in the same very characteristic membranous form described above.

In the many pure cultivations of *B. aceti* I have made, no form of growth in the least resembling in microscopic appearance the tough gelatinous film of the "vinegar plant" was ever observed; the surface zooglœa form of *B. aceti* being thin and easily broken up by the least agitation. The chemical reactions of the two growths are also entirely different; a cold solution of potash at once completely disintegrates the pellicle of *B. aceti*, but the "vinegar plant" membrane will withstand boiling with this solution for many hours

without appreciable change. The pellicle of *B. aceti* on treatment with concentrated sulphuric acid and iodine, gives no colour, but the "vinegar plant" is stained of a deep blue, similar reactions to these being also given by iodine dissolved in zinc chloride solution. Thus the membrane of the "vinegar plant" gives the characteristic reactions for *cellulose* (of which I shall show further on it is chiefly composed), whereas the zooglœa pellicle of *B. aceti* does not show any trace of this substance.

Previous writers who have described the membranous growth of the "vinegar plant" (*e.g.*, Zopf, *Die Spaltpilze*, p. 63, who evidently refers to it under the name "Essighautchen," and "Essigmutter"), have considered it to be a zooglœa form of *B. aceti;* but, from what I have said above, it will be seen that this is open to the strongest doubt. The true zooglœa form of *B. aceti* is an entirely different form, as I have just shown. Considering, therefore, that under so many different conditions of growth, the "vinegar plant" adheres to its one distinctive form, without ever approaching to that of *B. aceti*, and considering also that it develops a distinct chemical compound, cellulose, which appears to be entirely absent from *B. aceti*, it is impossible to come to any other conclusion than that the two organisms are specifically distinct.

When a membrane of the "vinegar plant" is examined microscopically, it is found to consist of bacteria, arranged more or less in lines, and lying embedded in a transparent structureless film. These bacteria are most commonly found as rods about 2 μ in length, several often being united together. The divisions, however, are readily seen when the growth is dried and stained with aniline-violet, which brings out the bacteria very distinctly, as the membrane in which they lie remains colourless. In old cultivations, the rods are often to a large extent replaced by micrococci about 0·5 μ in diameter (? spores). Sometimes, and more especially when the ferment has been grown in an unsuitable nourishing medium, like yeast-water, it appears as long twisted threads from 10—30 μ in length, and of a leptothrix nature. I have never observed with this ferment the peculiarly swollen involution forms so frequent in old cultivations of *B. aceti*. In the upper surface of an old membrane of the "vinegar plant," and also in the membrane grown on the surface of solid gelatin, cells are often found whose sides are much distended, and contain one or two highly refrangent nuclei resembling spores in appearance. These nuclei (or spores) are deeply stained by aniline dyes, and are often found free from any envelope.

In the liquid in which a membrane of ferment is growing, a few free swimming cells are always to be found, particularly if the membrane has been shaken, but these cells on cultivation always reproduce the membranous growth.

A temperature of about 28° appears to be most favourable to the growth of the "vinegar plant." Above 36°, it refuses to grow, but still lives.

The fermentations produced by this ferment show the same chemical changes as those produced by *B. aceti*, so far as I have investigated them. Ethylic alcohol is oxidised by it to acetic acid, and the acid so formed is afterwards entirely broken up. Dextrose is oxidised to gluconic acid; and lævulose is also formed from mannitol. Like *B. aceti* also, it has no fermentative action upon cane-sugar, starch, or lævulose. These results were arrived at in a similar manner to those obtained with *B. aceti*, and fully described in my previous paper, it is therefore needless to describe them further.

The great chemical difference between the "vinegar plant" and *B. aceti* is, as we have seen above, the presence of a membrane holding together the cells of the ferment, and which gives the usual reactions for cellulose. In order to ascertain with certainty the chemical composition of this substance, I proceeded in the following manner. A membrane of the ferment was taken, and after well washing with hot water, was boiled for 20 minutes with a 10 per cent. solution of caustic potash. This treatment did not appreciably affect the gelatinous film, but the bacteria embedded in it were disintegrated. After washing the film with dilute hydrochloric acid, and afterwards with water, it was treated with a solution of bromine, according to Müller's process for obtaining pure cellulose. After following out this method, the final product was a colourless semi-transparent film, retaining the shape and gelatinous character of the original membrane. When examined under the microscope, no trace of structural form could be detected. On treating a portion with ammonio-cupric oxide solution, it dissolved with ease, and the filtered solution, when acidified with hydrochloric acid, gave a precipitate exactly similar to that from the cellulose of cotton-wool when treated in a similar manner. Strong sulphuric acid dissolved the membrane without blackening, and on diluting the solution with water and boiling, a sugar was formed which reduced Fehling's solution.

A portion of the membrane was dried at 105°, and 0·2302 gram weighed out, and burnt with chromate of lead. This yielded 0·3737 gram CO_2 and 0·1295 gram OH_2. On calculation this gives—

		Cellulose $(C_6H_{10}O_5)_n$.
C..........	44·26	44·44
H..........	6·25	6·17
O..........	49·49	49·39
	100·00	100·00

This analysis, together with the reactions mentioned above, leave no doubt that the membrane of the "vinegar plant" is *cellulose.* As the cellulose in a fresh membrane of the ferment is easily dissolved by ammonio-cupric oxide, this, according to Fremy and Urbain (*Compt. rend.*, **93**, 926), shows it to be cellulose proper, like that of cotton-wool; metacellulose, usually found in fungi, is insoluble under similar circumstances, even after treatment with acids. The envelope of yeast cells, usually said to be cellulose, is (according to Liebig) also insoluble in ammonio-cupric oxide.

A different ferment from the one with which we are now concerned, and known as *Leuconostoc mesenterioïdes*, is described as being enveloped in a gelatinous membrane somewhat similar in appearance to the membrane of the "vinegar plant;" but Scheibler has shown that this body is an insoluble modification of the gum, dextran, and decomposable by alkalis into the soluble form. I have examined both the membrane of the "vinegar plant," and also the solution in which it grows, but can find no trace of dextran.

Quantitative estimations (by Müller's process) of the cellulose in membranes of the "vinegar plant," grown under various conditions, show that it varies from 35 to 62 per cent. when calculated on the total weights of the original membranes dried at 100°.

This production of cellulose by a simple cell plant, and its use as a cell connecting medium, seems of great interest in view of the important part which cellulose plays in a similar manner in the more highly organised forms of the vegetable kingdom; and it appeared that any information that could be gained, as to the materials from which cellulose is formed by the "vinegar plant," might perhaps assist in better understanding the complex reactions which go on in the higher plants. To this end, my first experiments were made by inoculating the "vinegar plant" into sterilised solutions of Pasteur's mineral medium, containing respectively 3 per cent. of cane-sugar, dextrose, starch, and alcohol. These solutions were kept at a temperature of 28° for six weeks, but, with the exception of the solution containing dextrose, no growth took place. The dextrose solution developed a small but well-marked growth of the membrane. This set of experiments gives fairly good proof that dextrose can be converted into cellulose by the ferment; but the negative proof concerning cane-sugar, starch, and alcohol, is weak, as some cause other than the inability of these compounds to be converted into cellulose, might have prevented the ferment from growing. In order to get over this difficulty, recourse was had to yeast-water, in which solution the ferment is able to grow, but only, as I have stated above, in a very weak form. 1 gram of each of the carbohydrates to be used (viz., cane-sugar, dextrose, and starch), was dissolved in 100 c.c. of

the same preparation of yeast-water, sterilised, and inoculated with the ferment; and at the same time two flasks, containing 100 c.c. each of the yeast-water alone, were inoculated. After 16 days, the flasks were opened and examined; the flask containing dextrose had developed a thick white membrane on the surface, but all the others showed a transparent jelly-like growth in the body of the liquid. The films of ferment in all the experiments were then removed carefully, and after washing with water, were treated with dilute potash and afterwards by Müller's process, in the manner described above. The pure cellulose films thus obtained were then dried at 100°, and weighed, with the following results:—

	Weight of cellulose.
Dextrose and yeast-water	0·0227 gram.
Starch and yeast-water........	0·0067 ,,
Cane-sugar and yeast-water	0·0080 ,,
Yeast-water alone No. I........	0·0053 ,,
,, ,, No. II	0·0052 ,,

In considering these experiments, it is evident, from the extremely close agreement of the weight of cellulose derived from the two solutions of yeast-water alone, that 5·2 mgrms. may safely be taken as the amount due to the yeast-water when the ferment had developed in it. We can therefore fairly deduct this from the weights found in the other experiments, and thus ascertain how far the carbohydrates contained in the solutions may have been converted into cellulose. Thus we find that 17·5 mgrms. of cellulose had been formed from dextrose, whilst only 1·5 mgrms. of cellulose had been formed in the starch solution, and 2·8 mgrms. in the cane-sugar solution. These latter quantities are so very small, that when we consider that it is very difficult to obtain starch quite pure, and that the cane-sugar used is sure to have been slightly inverted by the repeated boilings necessary for sterilisation, I think we may safely conclude that the "vinegar plant" is unable to convert either starch or cane-sugar into cellulose, even when growing freely in their presence. The weight of the cellulose formed in the dextrose solution quite confirms the first experiment with Pasteur's solution, in showing that the ferment can convert this sugar into cellulose. The experiments I have just described are only one series out of two which I made, both of which pointed to a similar conclusion.

The formation of cellulose from dextrose by the ferment is noteworthy, as we have here a case of a simple cell having two totally distinct actions on the same chemical compound; for, as I have before said, the fermentative action of the cell upon dextrose is to produce gluconic acid by a fixing in some way of the oxygen of the air, whilst

it also has the power of constructing the more complex molecule, cellulose, from the same substance. It is of course impossible to determine whether any one cell has these two powers at the same time, but I have determined by experiment that during the time that the cellulose membrane is growing, gluconic acid is formed.

The formation of cellulose by the "vinegar plant" from the carbohydrates must not be looked on as an act of fermentation, as it is evidently only a product of assimilation formed for the special use of the plant itself.

A series of experiments carried on in a manner similar to the one I have just described, was made to ascertain the action of the ferment on mannitol and on lævulose, the results of which are shown in the following table. 100 c.c. of the same yeast-water was used in each experiment:—

No.		Total weight of film, dried at 100°.	Cellulose in film, dried at 100°.	Per cent. of cellulose in film.
1	Dextrose ($C_6H_{12}O_6 + OH_2$), 2 grams..................	0·0339	0·0172	50·74
2	Mannitol ($C_6H_{14}O_6$), 2 grams..	0·1755	0·0948	54·02
3	Lævulose from inulin, 2 grams.	0·1777	0·1060	59·65
4	Lævulose from mannitol, 2 grams	0·1643	0·1015	61·17
5	Yeast-water alone............	—	0·0038	—

It is evident, from the above experiments, that mannitol and lævulose are far more favourable to the growth of the ferment than dextrose, and also that cellulose is formed from them more freely.

During the growth of the ferment in lævulose solutions, no trace of fermentative action was observed (neither acid nor alcohol was formed). In Experiment 4, an estimation of the lævulose was made in the solution with the polariscope, both before and after the growth of the membrane. 0·314 gram of lævulose had disappeared, whilst a membrane of ferment weighing 0·1643 gram, and containing 0·1015 gram of cellulose, had grown in the liquid. Not less than 0·113 gram of the sugar disappeared would be required for the formation of the cellulose found, the remainder being probably used for the growth of the ferment cells. The great difference between this experiment with lævulose and the experiment with dextrose—where true fer-

mentation had been going on—will be evident by comparing the results of the analyses of No. 1 experiment with the above.

Here 1·111 gram of dextrose was decomposed, 0·720 gram of which was found as gluconic acid, the remainder having gone for the production of cellulose, food for the cells, &c. Yet—notwithstanding active fermentation having been carried on—the total weight of the ferment formed was only about one-fifth of that found when the ferment grew in a solution of lævulose, although no fermentation was apparent in the latter experiment. This seems to raise a question as to whether the "vinegar plant" derives any benefit itself from the oxidising fermentative power it possesses when grown in presence of dextrose, alcohol, &c., and whether this property may not be something entirely unconnected with the necessities of its growth. My experiments appear to show the possibility of such being the case, and I intend to investigate these actions further.

During the growth of the ferment in presence of mannitol, this substance is converted into lævulose; it is therefore not possible to say that mannitol itself can be converted directly into cellulose.

An experiment was made to ascertain if ethylic alcohol took part in the growth of the cellulose membrane of the "vinegar plant." In this experiment the ferment was grown in yeast-water containing 4 per cent. of alcohol; a cultivation being made in yeast-water alone at the same time. At the end of the experiment, the same weight of cellulose had been formed in both cases, thus showing that alcohol took no part in its formation. In the alcoholic solution, 1·20 gram of acetic acid was found.

The "vinegar plant" is frequently used in country places for the manufacture of home-made vinegar, by introducing a membrane of the ferment into a solution of coarse brown sugar. As a pure cultivation of this ferment has no action on cane-sugar, I procured a membrane that had been used for the purpose described above to examine its action. Microscopic examination showed the ferment to be much contaminated with ordinary yeast cells (*Saccharomyces cerevisiæ*). On introducing a portion into a cane-sugar solution, the yeast cells present inverted and fermented the sugar, forming alcohol which, after the first fermentation had ceased, was oxidised to acetic acid in the ordinary way by the growth of a membrane of the vinegar plant on the surface of the solution.

The "vinegar plant" has no distinctive scientific name, I therefore suggest, in consideration of its power of forming cellulose, that *Bacterium xylinum* would be a suitable name for this ferment.

XLIV.—*Paranitrobenzoylacetic Acid and some of its Derivatives.*

By W. H. PERKIN (Jun.), Ph.D., and GUSTAV BELLENOT, Ph.D.

IN previous researches on ethylic benzoylacetate, it has been shown that it is not only capable of entering into almost all the reactions in which ethylic acetoacetate takes part, but moreover has the great advantage that its derivatives, being aromatic substances, have a much greater tendency to crystallise than those of the acetoacetate.

During the study of some of the more complicated derivatives of ethylic benzoylacetate, and more especially the benzoyl-derivatives of trimethylene and tetramethylene, it was found necessary, in order to explain the formation of these compounds, that not only the acids themselves, but also their ethereal salts should be solid, but this is not always the case when ethylic benzoylacetate is employed.

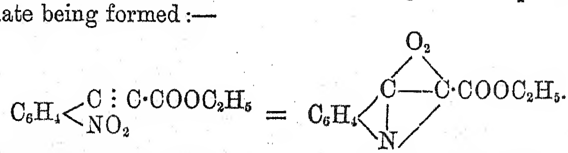
It seemed, therefore, if a nitro-derivative of ethylic benzoylacetate could be employed as the starting point instead of the ethyl salt itself, that this difficulty could be avoided, and such is, in fact, the case.

Experiments were first made with the object of nitrating ethylic benzoylacetate directly, but as it is difficult to obtain the latter free from acetophenone, benzoic acid, and other impurities, no satisfactory results could be obtained, and this mode of procedure was abandoned.

It was, however, soon discovered that paranitrobenzoylacetic acid could easily be prepared by a process analogous to that for the formation of benzoylacetic acid from phenylpropiolic acid; that is, by treating paranitrophenylpropiolic acid with concentrated sulphuric acid:—

$$\underset{\text{Paranitrophenylpropiolic acid.}}{NO_2\cdot C_6H_4\cdot C:C\cdot COOH} + H_2O = \underset{\text{Paranitrobenzoylacetic acid.}}{NO_2\cdot C_6H_4\cdot CO\cdot CH_2\cdot COOH}$$

This fact is all the more interesting when it is remembered that ethylic orthonitrophenylpropiolate behaves so differently when treated in the same way. Baeyer (*Ber.*, **14**, 174), who studied this reaction, has shown that on treating the ortho-derivative with sulphuric acid, a simple intramolecular change takes place, ethylic isatogenate being formed:—



Ethylic orthonitrophenyl-propiolate. Ethylic isatogenate.

It seemed of interest, therefore, to prepare some of the derivatives of paranitrobenzoylacetic acid, an account of which we now desire to lay before the Society.

We have divided this research into the following sections :—

(1.) Paranitrophenylpropiolic acid.
(2.) Paranitrobenzoylacetic acid.
(3.) Methylic paranitrobenzoylacetate.
(4.) Methylic benzylparanitrobenzoylacetate.
(5.) Ethylic paranitrobenzoylacetate.
(6.) Ethylic nitrosoparanitrobenzoylacetate.
(7.) Ethylic ethylparanitrobenzoylacetate.
(8.) Ethylic allylparanitrobenzoylacetate.
(9.) Ethylic di-paranitrobenzoylsuccinate.

(1.) *Paranitrophenylpropiolic Acid.*

Paranitrocinnamic acid and its derivatives were first carefully examined by Drewsen (*Annalen*, **212**, 150).

If this acid is treated with bromine, it easily takes up 1 mol. Br exactly in the same way as cinnamic acid does, and is converted into paranitrophenyldibromopropionic acid, $NO_2\cdot C_6H_4\cdot CHBr\cdot CHBr\cdot COOH$. If this dibromo-acid is treated with alkalis, a curious reaction takes place, no α- or β-monobromo-acid being formed as in the case of dibromophenylpropionic acid, but the dibromide is split up partly into paranitrophenylpropiolic acid and partly into the original paranitrocinnamic acid, bromine being given off. In preparing paranitrophenylpropiolic acid by this method, the separation of these two acids is not only a matter of considerable difficulty, but the yield of acid obtained is very small. It was found, however, that better results could be obtained by using the dibromide of the ethereal salt instead of the free acid.

The following method of preparation is based on that proposed by Drewsen :—

Ethylic paranitrophenyldibromopropionate is first prepared by mixing pure ethylic paranitrocinnamate with a slight excess of bromine. On pounding the substances together, the ethereal salt dissolves in the bromine, and in a short time the whole solidifies to a brown cake of impure ethylic paranitrophenyldibromopropionate. This is reduced to powder, spread out in the air till the excess of bromine has evaporated, and then crystallised once from alcohol. In this way it is obtained quite pure in colourless crystals, and can be used directly for the preparation of paranitrophenylpropiolic acid.

For this purpose, the crystals are dissolved in a small quantity of

boiling alcohol, and the calculated amount of a hot alcoholic potash solution poured in until the mixture has a decidedly alkaline reaction. As soon as the reaction is finished, a slight excess of potash causes the solution to become brownish coloured, probably from the formation of azo-derivatives. After remaining for an hour or so, about twice the volume of water is added, the whole filtered, and the paranitrophenylpropiolic acid precipitated by acidifying with dilute sulphuric acid.

The precipitate being very difficult to collect, it is better to agitate the whole repeatedly with ether. By this means also a purer product is obtained, as the paranitrocinnamic acid which is always formed during the reaction is not dissolved by the ether. The ethereal solution is well washed with water and shaken with dilute potash solution, when the paranitrophenylpropiolic acid dissolves, leaving the paranitrophenylacetylene and paranitroacetophenone—which are always present—in the ethereal solution. The acid is then reprecipitated from the aqueous potash solution and again extracted with ether.

On distilling off the ether, the paranitrophenylpropiolic acid is obtained pure in small needles, and can be used directly for the preparation of paranitrobenzoylacetic acid.

(2.) *Paranitrobenzoylacetic acid.*

In order to prepare ethylic paranitrobenzoylacetate, experiments were first made on the action of sulphuric acid on ethylic paranitrophenylpropiolate. 50 grams of the pure ethereal salt were dissolved in 2 kilos. of concentrated sulphuric acid which had been diluted with about 40 c.c. of water, and the whole allowed to remain for several hours at the ordinary temperature. As no reaction appeared to take place at this temperature, experiments were made with a view of ascertaining the proper conditions for the transformation, and it was ultimately found that the addition of water took place best at 35—40°, and required at least 12 to 15 hours before the reaction was completed. On pouring the product on to ice, a dirty whitish flocculent precipitate was formed, which was collected, well washed with water, and dried on a porous plate. The addition of a drop of ferric chloride to the alcoholic solution of this substance gave a beautiful violet coloration, a proof that the reaction had really taken place.

It was soon discovered, however, that the compound formed was not the ethereal salt of paranitrobenzoylacetic acid, but the acid itself, the ethereal salt having undergone hydrolysis by the action of the sulphuric acid. All attempts to obtain the ethereal salt directly were in vain.

As the yield of acid obtained in this way was not good, it was necessary in order to be able to prepare larger quantities to improve the method. After numerous experiments, the following—which we give in detail—was found to give the best results.

Pure paranitrophenylpropiolic acid (50 grams) is dissolved in 2—3 kilos. of 80—85 per cent. sulphuric acid, and the whole kept at a temperature of 35—40° for 15 hours. The solution which is at first yellowish-coloured becomes darker and darker, and is at last of a deep brown. In order to determine whether the reaction is finished a sample is taken out, mixed with ice and water, and extracted with ether. The residue left on distilling off the ether is dissolved in dilute ammonia and boiled for about two minutes; this causes the separation of oily drops of paranitroacetophenone, which on cooling become solid and can be filtered off. On acidifying the filtrate, any unchanged paranitrophenylpropiolic acid is precipitated, and from the amount of this it is easy to judge how far the reaction has progressed.

When it is found that the reaction is finished, the product is poured on to ice. This causes the paranitrobenzoylacetic acid to be precipitated in whitish flakes, which must be removed from the acid liquid as rapidly as possible by extraction with ether. The ethereal solution is well washed with water, dried over calcic chloride, and the ether distilled off until crystals begin to form; these consist of nearly pure paranitrobenzoylacetic acid. The filtrate from these crystals contains, besides this acid, unchanged paranitrophenylpropiolic acid and paranitroacetophenone; these can be separated by recrystallisation from benzene. Pure paranitrobenzolyacetic acid crystallises from this solvent in almost colourless microscopic needles.

Analysis :—

I. 0·2511 gram substance gave 0·0840 gram H_2O and 0·4698 gram CO_2.

II. 0·2293 gram substance gave 13·2 c.c. N at 16° and 720 mm.

III. 0·3165 ,, ,, ,, 19·0 c.c. N at 13° and 709 mm.

	Found.				Theory. $NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}CH{\cdot}COOH$.
	I.	II.	III.		
C....	51·02	—	—	per cent.	51·19 per cent.
H ...	3·72	—	—	,,	3·34 ,,
N....	—	6·35	6·61	,,	6·69 ,,

This acid is formed from paranitrophenylpropiolic acid according to the equation—

$$NO_2{\cdot}C_6H_4{\cdot}C : C{\cdot}COOH + H_2O = NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}CH{\cdot}COOH.$$

Paranitrobenzoylacetic acid melts at 135°, being at the same time decomposed into paranitroacetophenone and carbonic anhydride. It is easily soluble in alcohol, ether, bisulphide of carbon, and light petroleum, more sparingly in benzene. The alcoholic solution gives an intense reddish-brown coloration with ferric chloride.

If the finely powdered acid is warmed with water at 60°, it dissolves in considerable quantity and without much decomposition, crystallising out on cooling in four-sided plates. The hot aqueous solution is coloured deep reddish-brown on the addition of ferric chloride, the cold saturated solution, however, only very slightly so.

When boiled with water or dilute acids, the acid is rapidly decomposed into carbonic anhydride and paranitroacetophenone:—

$$NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2{\cdot}COOH = NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}CH_3 + CO_2.$$

The preparation of pure salts of paranitrobenzoylacetic acid is a matter of great difficulty owing to their instability. The acid dissolves easily in dilute alkalis, with an intense yellow colour, the solution, however, soon becomes filled with needles of paranitroacetophenone.

The solution of the sodic salt was prepared by carefully neutralising the solution of the acid in sodic carbonate with dilute nitric acid. On the addition of silver nitrate to this, a light yellow amorphous silver salt was obtained, which was very unstable, however, and on analysis gave approximate numbers only.

The copper salt is a light green amorphous salt, which explodes if heated in the dry state.

The other salts are also very unstable.

(3.) *Methylic Paranitrobenzoylacetate.*

The methylic salt of paranitrobenzoylacetic acid is easily obtained by suspending the pure acid in absolute methyl alcohol, and saturating with hydrochloric acid gas, the whole being well cooled during the operation. In a short time, the methylic salt begins to crystallise out in yellow needles. After remaining for 12 hours at as low a temperature as possible, the crystals are collected and well washed with methyl alcohol. By one recrystallisation from methyl alcohol, they are easily obtained pure.

Analysis:—

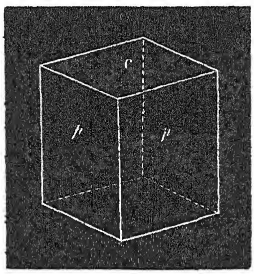
0·2360 gram substance gave 0·0926 gram H_2O and 0·4646 gram CO_2.

	Found.	Theory. $NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2{\cdot}COOCH_3$.
C.....	53·68	53·81
H.....	4·36	4·04

Methylic paranitrobenzoylacetate melts at 106—107°. It is only sparingly soluble in cold ethylic or methylic alcohol, but easily on boiling. It is easily soluble in light petroleum, benzene, and chloroform. The addition of a drop of ferric chloride to the alcoholic solution gives a brownish-violet coloration.

If the hot alcoholic solution of this ethereal salt be allowed to cool slowly, beautiful well-formed crystals can be obtained. For the following description of these I am indebted to the kindness of Professor Haushofer.

Methylic Paranitrobenzoylacetate.



Crystalline Form. Monoclinic.

$$a : b : c = 0{\cdot}4993 : 1\ (?).$$
$$\beta = 56^\circ\ 5'.$$

The crystals form the prismatic twinned combination $0P(c)$, $\infty P(p)$ in the direction of the vertical axis.

	Measured.
$p : p =$	$*135^\circ\ 0'$
$c : p =$	$*121^\circ\ 3'$

On the plane p, the angle made by the directions of extinction (with crossed Nicols) with the edge of the prism is about 15°.

Sodium compound, $NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}CHNa{\cdot}COOCH_3$.—If the solution of methylic paranitrobenzoylacetate (1 mol.) in warm alcohol is treated with the calculated quantity (1 mol.) of a strong solution of sodic ethylate or methylate, a dark orange-brown solution is formed, and, on stirring, the whole solidifies to a mass of yellow crystals. These after collecting, well washing with alcohol, and drying on a porous plate in a vacuum, gave the following numbers on analysis :—

0·2690 gram substance gave 0·0768 gram Na_2SO_4.

	Found.	Theory. $NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}CHNa{\cdot}COOCH_3$.
Na.....	9·27 per cent.	9·38 per cent.

The substance is, therefore, the monosodium-derivative of methylic paranitrobenzoylacetate. It is extremely stable, and behaves more like the salt of an acid than a sodium-derivative. It dissolves in water without decomposition, forming a yellow solution. It is scarcely attacked when treated with iodine.

(4.) *Methylic Benzylparanitrobenzoylacetate.*

It seemed to be of interest to determine whether the paranitro-derivatives of benzoylacetic acid could be used for synthetical experiments with the same advantage as benzoylacetic acid itself.

For this purpose, the action of benzyl chloride on the sodium-derivative of methylic paranitrobenzoylacetate was studied. The pure sodium-derivative was heated with the calculated quantity of benzyl chloride and a little alcohol in a sealed tube for six hours at 150°. The product was mixed with water, and once or twice extracted with ether. After drying the ethereal solution and distilling off the ether, a thick brownish oil remained, which did not solidify even when exposed for some days over sulphuric acid in a vacuum.

On distilling this crude product in a current of steam, a small quantity of oil passed over, but the main part remained behind in the retort. This was extracted with ether, and the ethereal solution well dried; on distilling off the ether, a thick oil remained, which, however, soon solidified to a cake of crystals. These were roughly purified by spreading them out on a porous plate, and then once or twice re-crystallising from dilute alcohol. Analysis:—

I. 0·1728 gram substance gave 0·4113 gram CO_2 and 0·0755 gram H_2O.

II. 0·3150 gram substance gave 13 c.c. N. $t = 11°$. Bar. = 710 mm.

	Found. I.	Found. II.		Theory. $NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}CH(C_7H_7){\cdot}COOCH_3$.
C......	64·91	—	per cent.	65·17 per cent.
H	4·86	—	,,	4·79 ,,
N......	—	4·57	,,	4·47 ,,

The substance was therefore methylic benzylparanitrobenzoylacetate, formed according the equation—

$$NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}CHNa{\cdot}COOCH_3 + C_7H_7Cl = NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}CH(C_7H_7){\cdot}COOCH_3 + NaCl.$$

It dissolves easily in most solvents, and crystallises from dilute alcohol in colourless plates which melt at 57°.

(5.) *Ethylic Paranitrobenzoylacetate.*

In order to prepare this ethereal salt, pure paranitrobenzoylacetic acid is suspended in an excess of absolute ethyl alcohol and the liquid thoroughly saturated with hydrogen chloride, care being taken that the temperature does not rise above 20° during the operation, otherwise decomposition is apt to set in. The product, which is a clear brownish liquid, is allowed to remain for two hours, and then poured into ice and water. This precipitates the ethereal salt in oily drops which solidify after a time; these can be collected on a filter, but it is best to extract the whole with ether. The ethereal solution, after washing with water, drying over calcic chloride, and distilling off the ether, deposits a thick brownish oil, which gradually solidifies on standing over sulphuric acid in a vacuum; this crude product can easily be separated from paranitroacetophenone and tarry products, by dissolving it in a little boiling alcohol.

On cooling, the ethylic paranitrobenzoylacetate crystallises out in yellow needles, which may be obtained almost colourless by repeated recrystallisation. The analysis gave the following results:—

I. 0·1619 gram substance gave 0·0672 gram H_2O and 0·3304 gram CO_2.

II. 0·1993 gram substance gave 10·50 c.c. N. $t = 12°$. Bar. = 709 mm.

	Found.			Theory.
	I.	II.		$NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2{\cdot}COOC_2H_5$.
C......	55·63	—	per cent.	55·64 per cent.
H.....	4·64	—	„	4·64 „
N......	—	5·83	„	5·90 „

Ethylic paranitrobenzoylacetate is easily soluble in boiling alcohol, much less so in the cold; it crystallises, however, best from a mixture of benzene (1 part), and light petroleum (b. p. 60—80°, 2 parts). If this solution be allowed to evaporate at the ordinary temperature, beautiful transparent crystals are obtained, melting at 74—76°. Professor Haushofer, who was kind enough to measure these, gave me the following account of them.

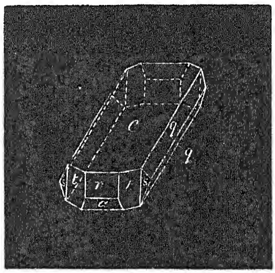
Crystalline Form. Monoclinic.

$$a : b : c = 0{\cdot}3584 : 1 : 1{\cdot}2380.$$
$$\beta = 72°\ 22'.$$

Tabular prismatic crystals developed in the direction of the clinodiagonal, with the combinations $0P(001) = c$, $P\!\!\!\!\backslash\infty(011) = q$, $\infty P\!\!\!\!-\infty(100) = a$, $-P\!\!\!\!-\infty(101) = r$, $-2P\!\!\!\!-2(121) = t$, $-4P\!\!\!\!\backslash4(141) = s$.

The surface c well developed but usually rough; the surfaces t and s usually very small, scarcely visible to the naked eye.

	Measured.	Calculated.
$c : a = (001)(100) =$	*107° 38′	— —
$q : q = (011)(0\bar{1}1) =$	*80 34	— — (above)
$c : r = (001)(101) =$	*121 52	— —
$t : r = (121)(101) =$	148 10	148° 40′
$s : r = (141)(101) =$	128 33	129 24
$q : a = (011)(100) =$	101 26	101 28



The plane of the optical axes is symmetrical. In convergent polarised light, the interference image of an axis makes its appearance on the surface c.

Ethylic paranitrobenzoylacetate dissolves fairly easily in sodic hydrate, especially on warming, producing a yellow solution. On the addition of acids, it is reprecipitated unchanged. Its alcoholic solution gives a beautiful brownish-violet coloration with ferric chloride.

Ethylic paranitrobenzoylacetate is easily reduced when treated with tin and hydrochloric acid in alcoholic solution, but the products formed have not been further examined.

If a strong solution of sodic ethylate (1 mol.) be added to the alcoholic solution of ethylic paranitrobenzoylacetate (1 mol.), an intense brownish-yellow solution is formed, which on standing solidifies to a mass of orange-coloured crystals of the sodium compound. These when collected, well washed with alcohol, and dried over sulphuric acid in a vacuum, gave the following numbers on analysis :—

0·2583 gram substance gave 0·0705 gram Na_2SO_4.

	Found.	Theory. $NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}CHNa{\cdot}COOC_2H_5$.
Na......	8·86 per cent.	8·88 per cent.

The dry sodium compound is characterised by its intensely bitter taste. It explodes feebly when heated, paranitroacetophenone and other compounds being formed.

It is sparingly soluble in cold water, but easily on warming, forming a deep yellow solution, which on the addition of an acid is instantly decolorised, ethylic paranitrobenzoylacetate being precipitated. If the solution of the sodium compound is mixed with a solution of an inorganic salt, the former is completely precipitated and the solution becomes colourless. The sodium compound is fairly easily soluble in boiling alcohol, and crystallises out on cooling in small orange-yellow needles, which are much redder than the sodium compound of methylic paranitrobenzoylacetate. The addition of ferric chloride to the alcoholic solution produces a dark reddish-brown coloration; but if this reagent is added to the solution of the sodium compound in water, a light reddish precipitate is formed, which appears to be crystalline, and is probably the *ferric* salt of ethylic paranitrobenzoylacetate.

If nitrate of silver is added to the solution of the sodium compound in water, a light yellow, amorphous precipitate is formed which explodes when heated in the dry state. The *lead* compound is easily obtained as a yellow amorphous mass, on adding a solution of acetate of lead to the aqueous solution of the sodium compound. The *copper* compound is a yellowish-green precipitate.

The compounds of ethylic paranitrobenzoylacetate with metals are remarkable for their stability. The sodium compound behaves exactly like the salt of an acid, it dissolves in water without decomposition and can even be recrystallised from it. The sodium compound of ethylic benzoylacetate is decomposed by boiling with water, and ethylic sodacetoacetate is split up when merely mixed with water. The sodium compound of methylic paranitrobenzoylacetate is, curiously enough, still more stable than that of the ethylic salt.

(6.) *Ethylic Nitrosoparanitrobenzoylacetate.*

As has been shown in previous researches (Trans., 1885, 244), ethylic benzoylacetate is easily converted into its isonitroso-derivative,

$$C_6H_5{\cdot}CO{\cdot}C(NOH){\cdot}COOC_2H_5,$$

when its solution in dilute sodic hydrate is treated with sodic nitrite and dilute sulphuric acid. This method, however, is not applicable to ethylic paranitrobenzoylacetate.

If the solution of the sodium compound of the ethereal salt is mixed with sodic nitrite, the former is precipitated almost entirely, and thus escapes the action of the nitrous acid when the mixture is acidified with dilute sulphuric acid.

After several experiments, however, it was found that the desired isonitroso-derivative could easily be obtained in the following way:—Pure ethylic paranitrobenzoylacetate is dissolved in dry ether and a

stream of nitrous gas passed through the solution until it is saturated, care being taken to cool well during the operation.

After standing for a short time, a rapid current of carbonic anhydride is passed through in order to remove the excess of nitrous acid as completely as possible, and the solution is allowed to evaporate spontaneously. The semi-solid mass which remains is first roughly separated from oily impurities by spreading it out on a porous plate, and then twice recrystallised from dilute alcohol.

Analysis :—

I. 0·1646 gram substance gave 0·0504 gram H_2O and 0·2980 gram CO_2.

II. 0·1927 gram substance gave 19 c.c. N. $t = 14°$. Bar. = 716 mm.

	Found. I.	Found. II.		Theory. $NO_2 \cdot C_6H_4 \cdot CO \cdot C(NOH) \cdot COOC_2H_5$.
C....	49·37	—	per cent.	49·62 per cent.
H ...	3·40	—	„	3·75 „
N ...	—	10·55	„	10·53 „

This compound is, therefore, ethylic nitrosoparanitrobenzoylacetate, formed according to the equation—

$$NO_2 \cdot C_6H_4 . CO \cdot CH_2 \cdot COOC_2H_5 + NO_2H = NO_2 \cdot C_6H_4 \cdot CO \cdot C(NOH) \cdot COOC_2H_5 + H_2O.$$

It is easily soluble in alcohol, ether, and acetone, less readily in benzene and light petroleum. It crystallises from dilute alcohol in colourless needles, which melt at 220° with decomposition. It dissolves easily in sodic hydrate, forming a deep yellow solution, and is reprecipitated unchanged on the addition of dilute acids.

(7.) *Ethylic Ethylparanitrobenzoylacetate.*

In preparing homologues of ethylic paranitrobenzoylacetate it is always better to start from the pure sodium compound than from the ethereal salt itself, as the products obtained in this way are always purer.

In order to prepare ethylic ethylparanitrobenzoylacetate, the pure sodium compound was heated with an excess of ethyl iodide and a little alcohol for about three hours at 100°. The whole was then evaporated to dryness on a water-bath, and the residue treated with water and extracted with ether. On distilling off the ether, a thick yellowish oil was left, which solidified after standing for some time over sulphuric acid in a vacuum. The crystals were first roughly freed from impurities by spreading the mass out on a porous plate, and then recrystallised twice from dilute alcohol.

Analysis :—

I. 0·1100 gram substance gave 0·0564 gram H_2O and 0·2365 gram CO_2.

II. 0·1512 gram substance gave 8 c.c. N. $t = 13°$. Bar. = 711 mm.

	Found. I.	Found. II.		Theory. $NO_2 \cdot C_6H_4 \cdot CO \cdot CH(C_2H_5) \cdot COOC_2H_5$.	
C....	58·63	—	per cent.	58·86	per cent.
H ...	5·69	—	„	5·66	„
N ...	—	5·50	„	5·28	„

Ethylic ethyl paranitrobenzoylacetate crystallises from dilute alcohol in colourless plates which melt at 39—40°. It is easily soluble in alcohol, ether, light petroleum, benzene, and carbon bisulphide.

All attempts to obtain the corresponding ethyl paranitrobenzoylacetic acid by hydrolysis were fruitless, paranitrobenzoic acid always being formed, even when very dilute potash was used. No better results were obtained with sulphuric acid at ordinary temperatures.

If ethylic ethylparanitrobenzoylacetate is heated with concentrated sulphuric acid at 100°, carbonic anhydride is given off, and, on adding water and extracting with ether, a yellowish oil is obtained; this on long standing becomes solid. It appears to be ethyl paranitroacetophenone, $NO_2 \cdot C_6H_4 \cdot CO \cdot CH_2 \cdot C_2H_5$.

The quantity was unfortunately too small for analysis.

(8.) *Ethyl Allylparanitrobenzoylacetate.*

This ethereal salt was prepared in exactly the same way as the ethylic ethylparanitrobenzoylacetate, allyl iodide being used instead of ethyl iodide. The crude product obtained was purified by repeated crystallisation from dilute alcohol.

Analysis :—

I. 0·2290 gram substance gave 0·1129 gram H_2O and 0·5100 gram CO_2.

II. 0·1695 gram substance gave 7·9 c.c. N. $t = 14°$. Bar. = 717 mm.

	Found. I.	Found. II.		Theory. $NO_2 \cdot C_6H_4 \cdot CO \cdot CH(CH_2 \cdot CH : CH_2) \cdot COOC_2H_5$.	
C....	60·72	—	per cent.	60·64	per cent.
H ...	5·47	—	„	5·41	„
N ..	—	5·08	„	5·05	„

Ethylic allylparanitrobenzoylacetate melts at 45—46°. A number

of experiments were made with the object of obtaining the corresponding allylparanitrobenzoylacetic acid, but without result; paranitrobenzoic acid always being formed. When heated with concentrated sulphuric acid at 100°, ethylic allylparanitrobenzoylacetate is decomposed into carbonic anhydride and a ketone, probably allylparanitroacetophenone, $NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH : CH_2$.

(9.) *Ethylic Diparanitrobenzoylsuccinate,*

$$\begin{array}{c} NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}CH{\cdot}COOC_2H_5 \\ | \\ NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}CH{\cdot}COOC_2H_5 \end{array}.$$

This compound is formed when the sodium-derivative of ethylic paranitrobenzoylacetate is treated with iodine:

$$2(NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}CHNa{\cdot}COOC_2H_5) + I_2 = \begin{array}{c} NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}CH{\cdot}COOC_2H_5 \\ | \\ NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}CH{\cdot}COOC_2H_5 \end{array} + 2NaI.$$

in a way exactly analogous to the formation of ethylic dibenzoylsuccinate from the sodium compound of ethylic benzoylacetate. To prepare it, the pure sodium compound of ethylic paranitrobenzoylacetate is first finely powdered and then agitated with an ethereal solution of iodine, containing the calculated quantity. If this solution be added by degrees, it will be seen that the colour of the iodine disappears rapidly at first, but at last only after long shaking, and it will be found usually that the whole amount is not decolorised. The product is then mixed with water and sulphurous acid, the ethereal solution separated, dried over calcic chloride, and evaporated. In this way, a yellow oil is obtained which, after standing over sulphuric acid in vacuum, deposits crystals. These must be separated from the oily mother-liquor by spreading out on a porous plate, and then recrystallised once or twice from dilute alcohol.

The analysis gave the following result:—

I. 0·2344 gram substance gave 0·0941 gram H_2O and 0·4805 gram CO_2.

II. 0·2001 gram substance gave 10·7 c.c. N. $t = 17°$. Bar. = 712 mm.

	Found.			Theory.
	I.	II.		$(NO_2{\cdot}C_6H_4{\cdot}CO)_2C_2H_2(COOC_2H_5)_2$.
C....	55·90	—	per cent.	55·93 per cent.
H...	4·48	—	,,	4·24 ,,
N...	—	5·82	,,	5·92 ,,

Ethylic diparanitrobenzoylsuccinate crystallises from dilute alcohol in colourless needles which melt at 180°. It is easily soluble in alcohol, ether, benzene, and light petroleum. If a solution of this substance in dry ether is mixed with an ethereal solution of sodic ethylate, a white amorphous compound is thrown down, which has without doubt the formula—

$$\begin{array}{l} NO_2\cdot C_6H_4\cdot CO\cdot CNa\cdot COOC_2H_5 \\ \qquad\qquad\qquad\quad | \\ NO_2\cdot C_6H_4\cdot CO\cdot CNa\cdot COOC_2H_5 \end{array}.$$

When ethylic diparanitrobenzoylsuccinate is treated with concentrated sulphuric acid, it is converted into a new compound, which is probably ethylic diparanitrophenylfurfurandicarboxylate. Owing to want of material, however, the reaction was not followed up.

From these experiments, it can be seen that ethylic paranitrobenzoylacetate may be used with advantage instead of ethylic benzoylacetate, the derivatives formed being solid and therefore easy to purify.

In a short time, we hope to be able to communicate to the Society the experiments on the formation of trimethylene- and tetramethylene-derivatives, which were made with this substance.

XLV.—*On the Vapour-pressures of Bromine and Iodine, and on Iodine Monochloride.*

By WILLIAM RAMSAY, Ph.D., and SYDNEY YOUNG, D.Sc.

So far as we know, the vapour-pressures of bromine and iodine have not been measured. The action of these elements on mercury precludes the ordinary method of experiment; but it is possible to use the method described by us in the Transactions, **47**, 42, substituting for the cotton-wool on the thermometer bulb a similar covering of asbestos, and interposing, between the still-apparatus and the manometer, a tube filled with solid sodium amalgam.

Although the vapour-pressures of these elements have not been determined, there are numerous isolated determinations of melting and boiling points; these, however, differ so widely from each other that a revision would seem desirable.

(1.) *Melting Point of Bromine.*—The following determinations have previously been made:—

Regnault	– 7·32°	Balard	– 18·0°	(freezing point).
Pierre	– 7·5	Serullas	– 18° to 20°	,,
Philipp	– 7·2 to – 7·3	Liebig	– 25·0°	,,
		Quincke	– 20·0	,,
		Baumhauer	– 24·5°	,,

Besides the statements of these authors, those of text-books are very contradictory: for example, Roscoe and Schorlemmer, $-21°$; Miller, $-12·5°$; Frankland, "Lecture Notes," $-20°$; Wurtz's Dictionary, freezing point $-22°$, melting point above $-12°$.

(2.) *Boiling Point of Bromine.—*

Pierre, 63·0° at 760·32.	Thorpe, 59·27° at 760.
Andrews, 58·0° at 760·0.	Bolas and Groves, 59·6° at 751·0.
Landolt, 58·6° at ?	

Besides these, Balard gives 47° and Löwig 45°, and one of these numbers is quoted in Williamson (47°).

(3.) *Melting Point of Iodine.—*

Regnault, 107°. During solidification, 113·6°.
Stas, 113—115°.

(4.) *Boiling Point of Iodine.—*

Regnault, 175° (about). Stas, above 200°.

Two sets of experiments were carried out with samples of bromine obtained from different sources. The first portion, after drying over sulphuric acid and boiling with potassium bromide to remove chlorine, distilled with absolute constancy from beginning to end at 57·65°* at 749·8 mm. The second sample was boiled with potassium bromide, dehydrated with phosphoric anhydride, and boiled, after a small quantity had come over, constantly at 58·85°, at a pressure of 755·8 mm. Both of these samples were tested for iodine with negative results; and on adding 0·25 per cent. of iodine to a portion of one of the samples, the boiling point was no longer constant. We are unable to account for this difference in boiling point in the two samples, which was found to be persistent throughout the whole range of pressures.

The results with the first sample are as follows:—(b. p. 57·65° at 749·8 mm.).

* All the temperatures were determined with a mercurial thermometer, but are corrected to express air-thermometer temperatures, for the mercurial thermometers had previously been carefully compared.

Series I.

Temperature.		Pressure.	Temperature.	Pressure.
Solid.	Liquid.		Liquid.	
− 18·44°	—	18·05 mm.	15·98°	147·4 mm.
− 11·65	—	32·0 ,,	19·30	174·35 ,,
− 11·59	—	32·85 ,,	19·92	175·45 ,,
− 7·25	—	45·55 ,,	28·23	255·2 ,,
—	− 5·1°	51·6 ,,	30·25	275·6 ,,
—	− 3·71	55·1 ,,	32·96	305·1 ,,
—	+ 0·19	67·8 ,,	35·68	340·9 ,,
—	3·95	82·5 ,,	38·57	379·8 ,,
—	5·28	88·05 ,,	41·47	421·4 ,,
—	10·44	112·95 ,,	44·24	465·0 ,,
—	10·52	113·35 ,,	46·86	511·3 ,,
—	15·59	143·7 ,,	49·22	558·3 ,,

Series II.

Temperature.		Pressure.	Temperature.	Pressure.
Solid.	Liquid.		Liquid.	
− 12·65°	—	28·2 mm.	12·63°	125·5 mm.
− 12·27	—	29·9 ,,	21·11	188·6 ,,
− 11·02	—	33·05 ,,	27·69	243·2 ,,
− 9·9	—	36·65 ,,	38·49	379·0 ,,
—	− 9·4°	39·70 ,,	44·60	474·3 ,,
—	+ 4·75	85·6 ,,	44·65	475·3 ,,

Repeated with sample 2 (b. p. 55·85 at 755·8 mm.).

	Temperature.	Pressure.	Temperature.	Pressure.
Liquid ..	− 9·88°	38·55 mm.	− 2·63°	57·9 mm.
Solid ..	− 9·68	35·55 ,,	− 0·31	65·25 ,,
,, ..	− 8·65	40·05 ,,	+ 10·4	111·8 ,,
Liquid ..	− 6·90	46·35 ,,	28·55	251·0 ,,
,, ..	− 5·04	50·9 ,,	47·65	518·2 ,,

With sample 1, series I, after the bromine had been frozen, on admitting air to raise the pressure, the temperature remained stationary at −7·05°; in series II, on solidification, the temperature rose from −9·45° to −7·45° and then fell again to −9·9°; and when the pressure was made to rise, the temperature again became stationary

at −7·0°. With sample 2, the temperature rose to −7·25° and then fell again. From direct observation, therefore, the melting point is seen to be between −7·0° and −7·45°.

As a comparison of these samples did not give concordant results, the second sample was first treated with caustic soda, evaporated, and the resulting bromate decomposed by heat. The bromine was recovered by distillation with potassium dichromate and dilute sulphuric acid. By this treatment all organic impurity must have been destroyed. The bromine was then digested with potassium bromide, and finally dried with sulphuric acid. It boiled constantly at 58·65° under a pressure of 757 mm.

A third sample, from a different source, was distilled alone, and boiled at 56·8—58·5° at 757 mm. It was then digested at the boiling point with potassium bromide, and allowed to stand over night; the boiling point was then 57·8° to 58·45° at 750·9 mm. It was then shaken with strong sulphuric acid and distilled at once, when it boiled from 58·35° to 58·5° at 750·9 mm.; and on standing for two days with strong sulphuric acid with occasional shaking, it boiled at 58·5° to 58·6° at 754·4 mm. This determination agrees with the result given by the purified sample, hence the last sample was used for experiment, and its vapour-pressures were measured. The rate of change of temperature at the boiling point of bromine is very nearly 1° for 25 mm.; corrected to 760 mm., the various determinations are as follows:—

First sample	58·05°
Second sample.....................	59·0
,, ,, after purification	58·75
Third ,, ...	58·75

The vapour-pressures of sample 3 were then determined.

Series I.

Temp.	Pressure.	Temp.	Pressure.	Temp.	Pressure.
− 7·87°	42·65 mm.	− 3·87°	53·8 mm.	+ 3·43°	80·35 mm.
− 7·0	45·7 ,,	− 2·40	57·8 ,,	5·45	87·8 ,,
− 5·74	49·1 ,,	− 1·06	62·2 ,,	7·55	97·65 ,,
− 4·69	51·5 ,,	+ 0·31	65·0 ,,	9·88	108·8 ,,
− 4·35	52·9 ,,	+ 2·03	73·95 ,,	12·31	127·25 ,,

Series II.

Temp.	Pressure.	Temp.	Pressure.	Temp.	Pressure.
− 17·12°	18·9 mm.	− 0·85°	63·2 mm.	28·80°	250·55 mm.
− 12·74	28·1 „	+ 2·78	75·75 „	32·70	293·4 „
− 12·70	27·65 „	6·38	91·7 „	34·68	321·0 „
− 10·36	34·85 „	14·30	133·65 „	36·98	350·25 „
− 6·39	47·05 „	20·96	181·25 „	38·61	375·75 „
− 4·79	51·0 „	22·20	189·75 „	—	—
− 2·02	59·0 „	25·72	220·25 „	—	—

Series III (with a Different Thermometer).

Temp.	Pressure.	Temp.	Pressure.	Temp.	Pressure.
34·4°	315·05 mm.	45·50°	478·2 mm.	54·1°	636·1 mm.
37·44	357·0 „	48·7	540·5 „	56·0	689·0 „
41·85	418·6 „	50·2	567·3 „	—	—

The boiling point was again determined, and was found to be 58·7° at a pressure of 759·1 mm. The melting point was also directly observed twice, it was −7·1°.

On considering these results, we think that the evidence goes against the first sample, inasmuch as the second sample, after purification, had a boiling point identical with that of the third.

The results of the vapour-pressures of the third sample are represented as a curve (No. 1), and it will be seen that the curve representing the vapour-pressures of the solid is not continuous with that of the liquid, and that the two curves intersect at a point corresponding to a temperature of −7·1°, and a pressure of 44·5 mm.

The ratios of the absolute temperatures of bromine and water at equal vapour-pressures were calculated, and are given in the following table. The value of c in the formula $R' = R + c\ (t' - t)$ is for liquid bromine −0·000586, and for solid bromine + 0·00114. (See *Phil. Mag.*, 1886, p. 33.)

Ratios of Absolute Temperatures of $\dfrac{Water}{Bromine}$.

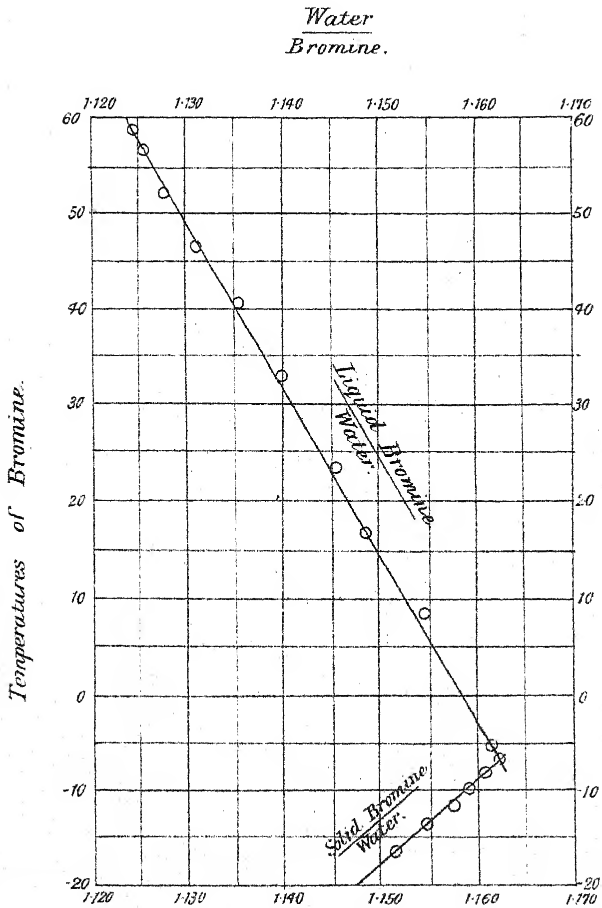
	Pressure.	Temp. of water.	Temp. of bromine.	Ratio.
Solid	20 mm.	273 + 22·3°	273 − 16·65°	1·1519
,, ...	25 ,,	,, 26·0	,, 14·0	1·1544
,, ...	30 ,,	,, 29·1	,, 12·0	1·1575
,, ...	35 ,,	,, 31·8	,, 10·05	1·1592
,, ...	40 ,,	,, 34·2	,, 8·4	1·1610
,, ...	45 ,,	,, 36·3	,, 7·0	1·1628
Liquid ..	50 ,,	,, 38·3	,, 5·05	1·1618
,, ...	100 ,,	,, 51·7	,, + 8·20	1·1547
,, ...	150 ,,	,, 60·1	,, 16·95	1·1488
,, ...	200 ,,	,, 66·6	,, 23·45	1·1456
,, ...	300 ,,	,, 75·9	,, 33·05	1·1400
,, ...	400 ,,	,, 83·0	,, 40·45	1·1357
,, ...	500 ,,	,, 88·7	,, 46·8	1·1310
,, ...	600 ,,	,, 93·5	,, 51·95	1·1278
,, ...	700 ,,	,, 97·7	,, 56·3	1·1257
,, ...	760 ,,	,, 100·0	,, 58·75	1·1243

It will be seen that these ratios, mapped against temperatures of bromine (*see* Curve 2) give points in a straight line; in other words c is constant.

Vapour-pressures of Iodine.
Series I.

Solid.		Liquid.	
Temperature.	Pressure.	Temperature.	Pressure.
58·1°	4·9 mm.	114·1°	89·8 mm.
64·5	6·05 ,,	114·9	93·55 ,,
66·3	6·25 ,,	117·8	103·0 ,,
75·2	11·5 ,,	120·4	113·4 ,,
80·4	15·15 ,,	123·15	124·5 ,,
86·0	21·25 ,,	125·5	135·8 ,,
91·8	28·95 ,,	127·1	142·9 ,,
91·9	29·6 ,,	166·6	475·0 ,,
96·8	37·8 ,,	169·4	505·5 ,,
102·7	50·65 ,,	171·7	535·6 ,,
105·7	59·85 ,,	174·5	575·3 ,,
113·8	87·0 ,,	177·6	630·3 ,,
—	—	177·7	633·9 ,,
—	—	180·75	680·5 ,,
—	—	186·4	764·2 ,,
—	—	185·2	—
—	—	185·45	—
—	—	185·45	—
—	—	185·55	—

Ratio of Absolute Temperatures.



Ratios of Absolute Temperatures of $\frac{\textit{Water}}{\textit{Bromine}}$.

	Pressure.	Temp. of water.	Temp. of bromine.	Ratio.
Solid	20 mm.	273 + 22·3°	273 − 16·65°	1·1519
,, ...	25 ,,	,, 26·0	,, 14·0	1·1544
,, ...	30 ,,	,, 29·1	,, 12·0	1·1575
,, ...	35 ,,	,, 31·8	,, 10·05	1·1592
,, ...	40 ,,	,, 34·2	,, 8·4	1·1610
,, ...	45 ,,	,, 36·3	,, 7·0	1·1628
Liquid ..	50 ,,	,, 38·3	,, 5·05	1·1618
,, ...	100 ,,	,, 51·7	,, + 8·20	1·1547
,, ...	150 ,,	,, 60·1	,, 16·95	1·1488
,, ...	200 ,,	,, 66·6	,, 23·45	1·1456
,, ...	300 ,,	,, 75·9	,, 33·05	1·1400
,, ...	400 ,,	,, 83·0	,, 40·45	1·1357
,, ...	500 ,,	,, 88·7	,, 46·8	1·1310
,, ...	600 ,,	,, 93·5	,, 51·95	1·1278
,, ...	700 ,,	,, 97·7	,, 56·3	1·1257
,, ...	760 ,,	,, 100·0	,, 58·75	1·1243

It will be seen that these ratios, mapped against temperatures of bromine (*see* Curve 2) give points in a straight line; in other words c is constant.

Vapour-pressures of Iodine.
Series I.

Solid.		Liquid.	
Temperature.	Pressure.	Temperature.	Pressure.
58·1°	4·9 mm.	114·1°	89·8 mm.
64·5	6·05 ,,	114·9	93·55 ,,
66·3	6·25 ,,	117·8	103·0 ,,
75·2	11·5 ,,	120·4	113·4 ,,
80·4	15·15 ,,	123·15	124·5 ,,
86·0	21·25 ,,	125·5	135·8 ,,
91·8	28·95 ,,	127·1	142·9 ,,
91·9	29·6 ,,	166·6	475·0 ,,
96·8	37·8 ,,	169·4	505·5 ,,
102·7	50·65 ,,	171·7	535·6 ,,
105·7	59·85 ,,	174·5	575·3 ,,
113·8	87·0 ,,	177·6	630·3 ,,
—	—	177·7	633·9 ,,
—	—	180·75	680·5 ,,
—	—	186·4	764·2 ,,
—	—	185·2	—
—	—	185·45	—
—	—	185·45	—
—	—	185·55	—

Series II.

Solid.		Liquid.	
Temperature.	Pressure.	Temperature.	Pressure.
105·6°	61·8 mm.	127·4°	143·1 mm.
108·4	70·6 ,,	130·1	157·3 ,,
111·6	78·8 ,,	134·4	180·5 ,,
114·2	90·5 ,,	147·8	273·2 ,,
—	—	158·4	374·6 ,,
—	—	158·9	376·0 ,,
—	—	167·2	475·6 ,,
—	—	174·4	574·3 ,,
—	—	177·9	625·8 ,,
—	—	180·8	679·1 ,,

Liquid.					
Temp.	Pressure.	Temp.	Pressure.	Temp.	Pressure.
134·5°	179·9 mm.	153·6°	323·0 mm.	163·2°	425·9 mm.
138·6	211·7 ,,	156·2	340·8 ,,	165·8	456·9 ,,
141·1	227·1 ,,	156·5	344·2 ,,	168·0	486·6 ,,
143·0	241·0 ,,	156·6	346·1 ,,	168·2	488·6 ,,
147·7	273 0 ,,	158·9	369·1 ,,	171·9	536·3 ,,
150·2	300·4 ,,	159·6	385·2 ,,	174·2	581·6 ,,
150·7	302·4 ,,	160·4	395·8 ,,	175·0	583·8 ,,
151·6	305·3 ,,	160·7	399·0 ,,	175·3	586·8 ,,
153·2	321·2 ,,	—	—	—	—

These numbers are not so accordant as usual. The reason for this is that the stem of the thermometer being invisible through the iodine vapour, the vapour was always kept below the level of the mercury in the thermometer, and hence a correction, not always certain, had to be introduced for the expansion of the mercury in the stem. It should be stated that the temperatures of both bromine and iodine are those of an air thermometer, for the thermometer used was calibrated by a measurement of the vapour-pressure of water, and of the substances described in the Transactions, **47**, 640.

It may be noticed in this case also, that the curve expressing the relation of pressure to temperature for solid iodine is not a continuation of that for liquid iodine, but that they intersect at 114·3° and a pressure of 91 mm. This has been already experimentally proved by us for a number of substances (*Phil. Trans.*, 1884, Part II, 461).

The melting point was directly observed to be between 113·8° and 114·1°; and another observation gave 114·2°.

Ratios of Absolute Temperatures of $\frac{Iodine}{Water}$.

	Pressure.	Temp. of water.	Temp. of iodine.	Ratio.
Solid	20 mm.	273 + 22·0°	273 + 85·0°	1·2123
,,	30 ,,	,, 29·1	,, 92·2	1·2089
,,	50 ,,	,, 38·3	,, 102·15	1·2051
,,	70 ,,	,, 44·6	,, 109·05	1·2029
,,	90 ,,	,, 49·55	,, 114·15	1·2003
Liquid	100 ,,	,, 51·7	,, 117·0	1·2011
,,	150 ,,	,, 60·1	,, 128·9	1·2066
,,	200 ,,	,, 66·6	,, 137·05	1·2075
,,	300 ,,	,, 75·9	,, 150·7	1·2144
,,	400 ,,	,, 83·0	,, 160·9	1·2188
,,	500 ,,	,, 88·7	,, 169·05	1·2222
,,	600 ,,	,, 93·5	,, 176·0	1·2251
,,	700 ,,	,, 97·7	,, 182·0	1·2274
,,	760 ,,	,, 100·0	,, 185·3	1·2287

These points were mapped in the ordinary way. The value of c for liquid iodine is $+0·0003986$, and for the solid $-0·000407$. The two lines intersect one another at 114·3°, the melting point of iodine.

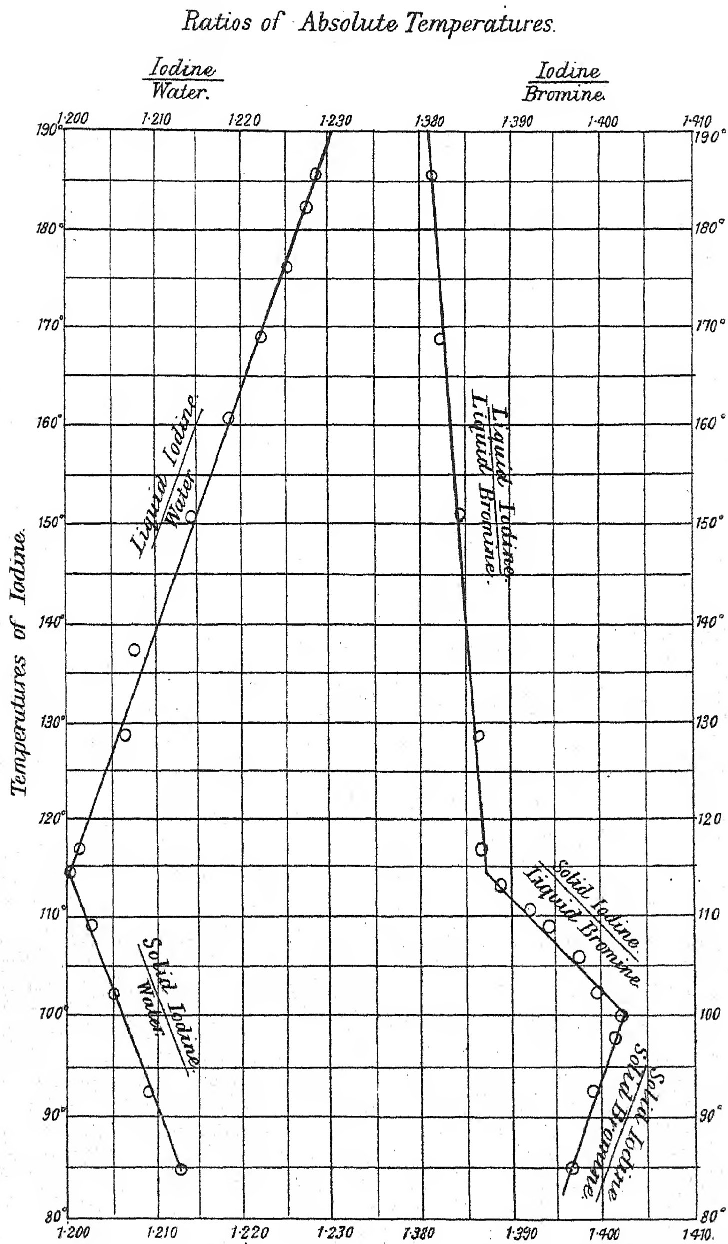
We have also constructed a diagram to show the ratios between the absolute temperatures at constant pressures of—

1. Liquid iodine ÷ liquid bromine, where $c = -0·000080$.
2. Solid ,, ÷ ,, ,, where $c = -0·001125$.
3. ,, ,, ÷ solid ,, where $c = +0·000413$.

In these cases the ordinates are the temperatures of iodine. The first two lines intersect at the melting point of iodine, and the second at a temperature of iodine, where iodine vapour exerts a pressure equal to that of bromine at its melting point. The points do not fall well in a straight line, owing probably to the difficulty we experienced in measuring the vapour-pressures of iodine.

From our results, the following data for the melting point of bromine are obtained:—

1. Highest temperature attained on solidification −7·45°.
2. Constant temperature during fusion, −7·0° and −7·05°, and with the third sample, −7·1°.
3. Intersection of vapour-pressure curves of solid and liquid, −7·05°.
4. Intersection of lines representing ratios for bromine and water, −7·0°.


Ratios of Absolute Temperatures.
Iodine / Water.
Iodine / Bromine.
1·200
1·210
1·220
1·230
1·380
1·390
1·400
1·410
190°
180°
170°
160°
150°
140°
130°
120°
110°
100°
90°
80°
Temperatures of Iodine.
Liquid Iodine / Water
Solid Iodine / Water
Liquid Iodine / Liquid Bromine.
Solid Iodine / Liquid Bromine
Solid Iodine / Solid Bromine.

irst result, $-7{\cdot}45°$, is of little value, inasmuch as the highest temperature is not necessarily attained on solidification. We that $-7{\cdot}05°$ expresses the true melting point very closely.

egards the boiling point of bromine at normal pressure, the ed number found by us is 58·0° for the first sample; that of ond and third samples is 58·7°; these numbers approximate se given by Andrews and by Landolt, 58·0° and 58·6° respec-; but that which we place most confidence in, 58·7°, differs from ound by Thorpe by 0·55°, and yet Thorpe's method of purifica-ppears unexceptionable. Thorpe's remark in his paper (*Chem. J.*, **37**, 172) on the thermal expansion of various bodies, that the solidifying point of the sample of bromine, viz., $-7{\cdot}5°$ to $-8°$, used ierre, points to its contamination with water is, however, quite unded on fact. The temperature to which a liquid can be cooled out freezing depends on various circumstances, and is not a fixed t; whereas the melting point, or the point of intersection of the our-pressure curves, is constant.

ne following data are available for the melting point of iodine :—

1. Direct observation, 114·1—114·3°.
2. ,, ,, 113·8—114·1°.
3. Intersection of vapour-pressure curves of solid and liquid, 114·3°.
4. Intersection of lines representing ratios for iodine and water, 114·3°.
5. Intersection of lines representing ratios for bromine and iodine, 114·05°.

The true melting point may be expressed by the number 114·15°, nich agrees well with that given by Stas, 113—115°, and with gnault, who found the temperature during solidification to be 3·6°.

The boiling point of iodine at 760 mm. pressure was found to be as mean of five direct observations, 184·61° at 764·2 mm.; corrected 760 mm. the temperature is 184·35°.

It was hoped by a study of the vapour-pressures of iodine monohloride to obtain results interesting on account of their comparison vith the constants of bromine. Iodine monochloride is, however, no stable substance. On distilling it at normal pressure, it dissociates, iving a sublimate containing trichloride, and while most of it boils t a temperature of 102°, the last portions boil as high as 106°, owing o the presence of free iodine. The vapour-pressure curve, therefore, btained by our usual method presents great irregularity; the iodine monochloride fractionates during measurement, and it is a matter of hance if two observations coincide. We spent a great deal of time over

this compound, and from the results obtained a curve was cons fitting the observed points as accurately as we were able to c On comparing the ratios between the absolute temperatures of monochloride and water, it was evident that the lines represent ratios of vapour-pressure of the solid should intersect that senting the ratios of the liquid; but the results were so irregul the point of intersection could not be observed. All that we c is that the value of c for the solid body is positive, whilst it is ne for the liquid.

Note.—Since writing this paper, a few measurements of the va pressures of solid iodine have been given by v. Richter (*Ber.*, 1060). His results corroborate ours in a remarkable manner. 20 mm. pressure he found a temperature of 85°; at 30 mm., 90°; 90 mm. at its melting point. Our numbers at these pressures 85° and 92·2°, and at the melting point we observed 89·8 mm. p sure. V. Richter, however, appears to be unaware of the fact we long ago made careful measurements of results which he gives the most part only qualitatively.

University College, Bristol.

XLVI.—*On the Action of Aldehydes and Ammonia on Benzil* (continued).

By Francis R. Japp, F.R.S., and W. Palmer Wynne, B.Sc.

Introduction.

The reactions of benzil with aldehydes and ammonia have as yet bee studied only in the case of aldehydes of the benzene series, and th same holds good with regard to the other diketones which have bee substituted for benzil in these reactions—phenanthraquinone and chrysoquinone. The reactions of another dicarbonyl-compound (glyoxal) with aldehydes and ammonia have, however, been studied in the case of fatty aldehydes by Radziszewski, who thus effected a new synthesis of homologues of glyoxaline.

In the present communication, we describe the reactions of benzil with fatty aldehydes and ammonia. We have also in one case employed a benzene-fatty aldehyde, cinnamaldehyde.

With fatty aldehydes, the reaction took place according to Equa-

tion II (Trans., 1884, 672) of the general reactions of this class, and substituted glyoxalines were obtained. Thus with acetaldehyde :—

$$\begin{array}{l} C_6H_5\cdot CO \\ \quad\;\; | \\ C_6H_5\cdot CO \end{array} + CH_3\cdot CHO + 2NH_3 = \begin{array}{l} C_6H_5\cdot C—NH \diagdown \\ \qquad\;\; \| \qquad\quad\;\; >C\cdot CH_3 \\ C_6H_5\cdot C——N \diagup\!\!\diagup \end{array} + 3H_2O.$$

Methyldiphenylglyoxaline.

A similar reaction occurred with isovaleraldehyde. Œnanthaldehyde, on the other hand, did not react with benzil and ammonia under the conditions of our experiment.

With cinnamaldehyde, two distinct reactions occur. A part of the substance reacts according to Equation III of the general reactions (*loc. cit.*, p. 673), thus :—

$$\begin{array}{l} C_6H_5\cdot CO \\ \quad\;\; | \\ C_6H_5\cdot CO \end{array} + 2C_6H_5\cdot CH : CH\cdot CHO + 2NH_3$$

$$= \begin{array}{l} C_6H_5\cdot CH : CH\cdot CH\cdot NH\cdot CO\cdot C_6H_5 \\ \qquad\qquad\qquad\quad | \\ C_6H_5\cdot CH : CH\cdot CH\cdot NH\cdot CO\cdot C_6H_5 \end{array} + 2H_2O.$$

Dibenzoyldicinnylenediamine.

This compound is analogous to that obtained from benzil, salicylaldehyde, and ammonia (*loc. cit.*), but unlike the salicylaldehyde compound, could not be converted into the non-benzoylated derivative. When heated with a solution of caustic potash in methyl alcohol, it parts with 1 mol. of benzoic acid, and is converted into an anhydro-base :—

$$\begin{array}{l} C_6H_5\cdot CH : CH\cdot CH—NH \diagdown \\ \qquad\qquad\qquad\quad | \qquad\qquad >C\cdot C_6H_5. \\ C_6H_5\cdot CH : CH\cdot CH——N \diagup\!\!\diagup \end{array}$$

Benzenyldicinnylenediamine.

This base, so far as we know, is the only compound yet prepared which contains the hydrogenated glyoxaline-complex—

$$\begin{array}{l} —CH—NH \diagdown \\ \quad\;\; | \qquad\quad\;\; >C— \\ —CH——N \diagup\!\!\diagup \end{array} .$$

A different hydrogenated glyoxaline-complex of the formula—

$$\begin{array}{l} —C—NH \diagdown \\ \quad\, \| \qquad\quad >CH— \\ —C—NH \diagup \end{array}$$

is, however, assumed to exist in amarine.

Another portion of the cinnamaldehyde above referred to reacts with benzil and ammonia in molecular proportions different from any hitherto observed in this class of reactions :—

$$2\begin{array}{l}C_6H_5\cdot CO\\ \quad| \\ C_6H_5\cdot CO\end{array} + C_6H_5\cdot CH:CH\cdot CHO + 2NH_3 = \underset{\text{Cinnimabenzil.}}{C_{37}H_{30}N_2O_3} + 2H_2O.$$

This, therefore, constitutes the *fourth* of the distinct reactions (cf. *loc. cit.*) in which aldehydes and dicarbonyl compounds jointly form condensation-products with ammonia. We shall show in a further communication (see following paper) that a similar reaction occurs when ammonia acts on benzil alone to form imabenzil,—nascent benzaldehyde, formed by the breaking up of a portion of the benzil, taking the part of the cinnamaldehyde in the foregoing equation. The reaction is probably, therefore, of more general application. The foregoing analogy has led us to name the compound $C_{37}H_{30}N_2O_3$ *cinnimabenzil.*

By treatment in the cold with a solution of potash in methyl alcohol, cinnimabenzil is decomposed, according to the equation—

$$\underset{\text{Cinnimabenzil.}}{C_{37}H_{30}N_2O_3} + KOH = \underset{\text{Cinnidimabenzil.}}{C_{30}H_{26}N_2O_2} + CH_5\cdot COOK.$$

When boiled with dilute sulphuric acid, it is decomposed as follows:—

$$\underset{\text{Cinnimabenzil.}}{C_{37}H_{30}N_2O_3} + 2H_2O = \underset{\text{Benzilimide.}}{C_{21}H_{17}NO_2} + \underset{\text{Cinnamaldehyde.}}{C_9H_8O} + \underset{\text{Benzoic acid.}}{C_7H_6O_2} + NH_3.$$

I. *Acetaldehyde and Ammonia with Benzil.*

20 grams of benzil and 8·5 grams of aldehyde were dissolved in a quantity of alcohol sufficient to keep the benzil in solution at 40°, and the warm liquid was then saturated with gaseous ammonia, after which the whole was allowed to remain for 24 hours. As nothing had separated at the end of that time, the solution was poured into water. A white flocculent substance was precipitated, which was thoroughly washed with water and then boiled with hot *dilute* hydrochloric acid, in which everything dissolved with the exception of a small quantity of resin. If the acid is too concentrated, the hydrochloride of the new base melts to an oil under the liquid, instead of dissolving. The base was precipitated by ammonia, and recrystallised from boiling benzene, which deposited it in tufts of minute colourless needles, with a constant melting point of 235°. It is practically insoluble in water, but dissolves readily in alcohol and in ether. From the solution in hot alcohol, it is deposited on cooling in well-formed crystals of the orthorhombic system (*vide infra*). These had a very faint yellowish tinge.

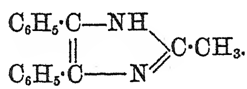
Analysis of a sample crystallised from benzene gave numbers agreeing with the formula $C_{16}H_{14}N_2$:—

	Substance.	CO_2.	H_2O.
I........	0·1138	0·3408	0·0628
II........	0·1177	0·3528	0·0640

III. 0·1076 gram, burnt with copper oxide in a vacuum, gave 21·91 c.c. of a mixture of nitrogen and nitric oxide, measured dry at 18°, and under 391·5 mm. pressure. After absorption of the nitric oxide there remained 21·91 c.c. of dry nitrogen at 17·8°, and under 365 mm. pressure.

	Calculated for $C_{16}H_{14}N_2$.		Found.		
			I.	II.	III.
C_{16}....	192	82·05	81·67	81·75	—
H_{14} ...	14	5·98	6·13	6·04	—
N_2....	28	11·97	—	—	11·95
	234	100·00			

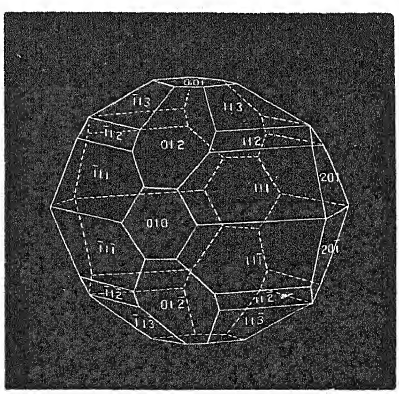
The constitutional formula of this compound, and the equation expressing its formation, have already been given. In accordance with this constitution, it would receive the name *methyldiphenylglyoxaline* :—



Mr. L. Fletcher has had the kindness to measure the crystals deposited from alcohol. He reports as follows :—

" *Methyldiphenylglyoxaline.*

COLOUR—Faintly yellow.



One crystal, about a millimetre in diameter, was measured.
SYSTEM—Orthorhombic.
ELEMENTS—$a : b : c :: 1.207 : 1 : 1.929$,
or $011 \cdot 010 = 27° 24' : 101 \cdot 001 = 57° 58\frac{1}{2}' : 110 \cdot 100 = 50° 21'$.
FORMS PRESENT—{010}{001}{012}{201}{111}{112}{113}.
DEVELOPMENT—*Vide* figure.

Angles.	Observed.	Calculated.
001·113	39° 55′—40° 23′	39° 52′
113·112	11° 16′, 11° 46′	11 32
112·111	16° 11′, 16° 19′	16 50
111·$\bar{1}$11	72° 27′	72 42
111·010	43° 40′—44° 16′	44 21
111·012	39° 55′—40° 19′	40 15
012·$\bar{1}$13	26° 18′, 26° 25′	26 29
001·012	43° 51′, 43° 56′	43 58
001·201	72° 22′—73° 32′	72 38
012·201	77° 27′—78° 2′	77 36
012·112	29° 54′, 29° 56′	29 55
111·201	47° 46′, 47° 49′	47 27"

Methyldiphenylglyoxaline is a monacid base. In a solution of the hydrochloride, platinic chloride (freed from excess of acid, which might otherwise cause a separation of hydrochloride) produces a yellow precipitate, consisting of microscopic needles of the formula $(C_{16}H_{14}N_2,HCl)_2PtCl_4 + 2H_2O$.

1·5446 grams of the air-dried salt lost on heating at 120° 0·0583 gram, and the resulting 1·4863 grams of anhydrous salt gave on ignition 0·3279 gram platinum.

	Calculated for $(C_{16}H_{14}N_2,HCl)_2PtCl_4 + 2H_2O$.	Found.
H_2O in 100 parts........	3·94	3·77

	Calculated for $(C_{16}H_{14}N_2,HCl)_2PtCl_4$.	Found.
Pt in 100 parts	22·17	22·06

The hydrochloride itself exhibits a peculiarity in its crystallisation, due probably to the formation of different hydrates. When the hot saturated solution is allowed to cool in an open vessel, the crystallisation starts from the surface of the solution at two or three points and proceeds in tufts of long silky needles, extending through the entire liquid. But if, on the other hand, the hot saturated liquid is corked up in a vessel so as to exclude the air, taking care that none of the needle-shaped crystals are left adhering to the cork or to the sides of the vessel, then the substance is deposited in granular crystals, which

begin growing within the liquid, and sometimes attain a considerable size. Neither long standing nor violent shaking suffices to start the crystallisation of needles in the closed vessel; but on removing the cork, this crystallisation of needles commences from the surface, showing that the liquid was still supersaturated with this form, and wherever the needles touch the transparent granular crystals, these become opaque, and are converted into aggregates of needles.

The behaviour of this salt recalls that of a solution of sodium sulphate saturated at the temperature of maximum solubility, and protected from the air.

II. *Isovaleraldehyde and Ammonia with Benzil.*

An alcoholic solution of 20 grams of benzil with 8·2 grams of isovaleraldehyde (boiling point 92—95°) was saturated with gaseous ammonia at 40°, and allowed to stand for 24 hours. The new compound separated in needles, and was filtered off. The mother-liquor on evaporation yielded a further quantity, together with some benzilimide (m. p. 139·5°; verified also by conversion into benzilam, m. p. 114°). It was purified by recrystallisation from benzene, which deposited it in silky needles, melting constantly at 223°; from hot alcohol, it separated on cooling in larger needles.

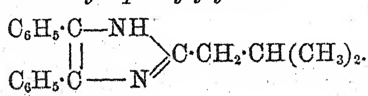
The analytical results agreed with the formula $C_{19}H_{20}N_2$:—

	Substance.	CO_2.	H_2O.
I........	0·1123	0·3396	0·0771
II........	0·1058	0·3196	0·0720

III. 0·1130 gram, burnt with copper oxide in a vacuum, gave 21·91 c.c. of a mixture of nitrogen and nitric oxide, measured dry at 17·5° and under 352 mm. pressure. After absorption of the nitric oxide there remained 21·91 c.c. of dry nitrogen at 17·5°, and under 323 mm. pressure.

	Calculated for $C_{19}H_{20}N_2$.		Found.		
			I.	II.	III.
C_{19}....	228	82·61	82·47	82·38	—
H_{20} ...	20	7·25	7·62	7·56	—
N_2....	28	10·14	—	—	10·16
	276	100·00			

The compound is *isobutyldiphenylglyoxaline* :—



The platinichloride,* $(C_{19}H_{20}N_2,HCl)_2PtCl_4$, was prepared by precipitation in the ordinary way, avoiding, however, the presence of free hydrochloric acid. It was thus obtained as an amorphous yellowish-brown precipitate, but small crystals separated from the mother-liquor on standing. The salt was anhydrous.

1·5956 grams dried at 100° gave on ignition 0·3222 gram platinum.

	Calculated for $(C_{19}H_{20}N_2,HCl)_2PtCl_4$.	Found.
Pt in 100 parts	20·23	20·19

III. *Cinnamaldehyde and Ammonia with Benzil.*

100 grams of benzil were dissolved in sufficient alcohol to keep the benzil in solution at 40°, 63 grams of cinnamaldehyde were added, and the whole was saturated with gaseous ammonia at 40°. While the gas was being passed in, a pulverulent white substance separated in considerable quantity, and was filtered off from the warm solution as soon as the saturation was complete. This compound was found to be practically insoluble in alcohol. The ammoniacal filtrate, on standing, deposited a large quantity of a flocculent white compound, which was soluble in alcohol. The filtrate from this compound yielded nothing crystallisable on evaporation.

Examination of the Compound Insoluble in Alcohol.—It was found that this compound dissolved readily in hot phenol, and was precipitated on the addition of three times the volume of alcohol as a crystalline powder, consisting of short microscopic prisms. After repeating this process of solution and precipitation several times, it was obtained with a constant melting point of 264°. The compound was boiled with successive portions of alcohol to remove the last trace of phenol and dried finally at 120°.

Analyses agreed with the formula $C_{32}H_{28}N_2O_2$:—

	Substance.	CO_2.	H_2O.
I........	0·1342	0·3991	0·0730
II........	0·1250	0·3720	0·0686

III. 0·1120 gram, burnt with copper oxide in a vacuum, gave 13·07 c.c. of a mixture of nitrogen and nitric oxide, measured dry at 17° and under 351·5 mm. pressure. After absorption of the nitric oxide, there remained 13·07 c.c. of dry nitrogen at 17° and under 318·5 mm. pressure.

* See footnote, Trans., 1884, p. 676.

	Calculated for $C_{32}H_{28}N_2O_2$.		Found. I.	II.	III.
C_{32}....	384	81·35	81·11	81·16	—
H_{28} ...	28	5·93	6·04	6·09	—
N_2....	28	5·93	—	—	6·08
O_2....	32	6·79	—	—	—
	472	100·00			

The yield of pure substance was 11 grams from 100 grams of benzil, but was greatly increased in a subsequent experiment by employing 2 molecular proportions of cinnamaldehyde to 1 of benzil.

The reaction in which this substance, *dibenzoyldicinnylenediamine*, is formed, and its constitutional formula, are given on p. 463. The action of various reagents on this compound was tried, but only with potash was a definite result obtained.

Action of Potash on Dibenzoyldicinnylenediamine.—When the compound was heated with a 10 per cent. solution of caustic potash in methyl alcohol in a sealed tube for three hours at 150°, it went into solution, and, on cooling, the liquid was filled with lustrous laminæ, probably potassium benzoate. On opening the tube, a smell of ammonia was perceptible. The contents of the tube were evaporated to a semi-solid state on a water-bath, mixed with water and filtered hot. The filtrate, on acidifying, gave benzoic acid. The brownish residue on the filter was dissolved in hot benzene, from which it was obtained, after two crystallisations, in small faintly yellow crystals with a constant melting point of 207°.

The results of analysis agreed with the formula $C_{25}H_{22}N_2$:—

	Substance.	CO_2.	H_2O.
I........	0·1246	0·3898	0·0763
II........	0·1317	0·4116	0·0806

III. 0·1085 gram, burnt with copper oxide in a vacuum, gave 13·79 c.c. of dry nitrogen at 23° and under 413·5 mm. pressure. Nitric oxide was not present.

	Calculated for $C_{25}H_{22}N_2$.		Found. I.	II.	III.
C_{25}....	300	85·71	85·32	85·24	—
H_{22} ...	22	6·29	6·80	6·80	—
N_2....	28	8·00	—	—	8·02
	350	100·00			

The compound, which we have named *benzenyldicinnylenediamine* (see p. 463), is formed from the dibenzoyl-compound by the abstrac-

tion of 1 mol. of benzoic acid. It may be regarded as an anhydro-base derived from the hypothetical monobenzoyldicinnylenediamine—

$$\begin{array}{l} C_6H_5{\cdot}CH : CH{\cdot}CH{\cdot}NH{\cdot}C\boxed{O}{\cdot}C_6H_5 \\ \qquad\qquad\qquad | \\ C_6H_5{\cdot}CH : CH{\cdot}CH{\cdot}N\boxed{H_2} \end{array}$$

by the abstraction of the elements of water.

When this base is boiled with hydrochloric acid, it is converted into a hydrochloride, but dissolves only very slightly. The hydrochloride is, however, soluble in alcohol. On the addition of aqueous platinic chloride to the alcoholic solution, the platinichloride separates in yellow silky needles of the formula $(C_{25}H_{22}N_2,HCl)_2PtCl_4 + 2H_2O$. The salt thus prepared was washed with alcohol, air-dried, and analysed.

0·9084 gram of the air-dried salt lost, on heating at 120°, 0·0282 gram, and the resulting 0·8802 gram of anhydrous salt gave, on ignition, 0·1540 gram of platinum.

	Calculated for $(C_{25}H_{22}N_2,HCl)_2PtCl_4 + 2H_2O$.	Found.
H_2O in 100 parts........	3·14	3·10

	Calculated for $(C_{25}H_{22}N_2,HCl)_2PtCl_4$.	Found.
Pt in 100 parts........	17·53	17·50

Examination of the Compound soluble in Alcohol.—The flocculent white compound (p. 468) from the benzil-cinnamaldehyde-ammonia reaction was dissolved in boiling alcohol. The solution deposited two sorts of crystals—slender needles and minute short prisms—which, however, proved to be merely different crystalline forms of the same substance, and could be converted one into the other by slightly varying the conditions of crystallisation. Both melted at the same temperature, 188°, and gave the same figures on analysis. Neither contained alcohol of crystallisation. The compound is also soluble in boiling benzene. The yield, using the proportions given on p. 468, is about one-tenth of the weight of benzil taken.

The analyses agreed with the formula $C_{37}H_{30}N_2O_3$:—

	Substance.	CO_2.	H_2O.
I........	0·1252	0·3701	0·0645
II........	0·1326	0·3918	0·0675

III. 0·1074 gram, burnt with copper oxide in a vacuum, gave 13·07 c.c. of a mixture of nitrogen and nitric oxide, measured dry at 17° C. and under 284·5 mm. pressure. After absorption of the nitric

oxide, there remained 13·07 c.c. of dry nitrogen at 17°, and under 269·5 mm. pressure.

IV. 0·1193 gram gave 13·07 c.c. dry nitrogen and nitric oxide at 17·4° and under 325 mm. pressure, and after absorption of the nitric oxide, 13·07 c.c. dry nitrogen at 17·2° and under 297·5 mm. pressure.

	Calculated for $C_{37}H_{30}N_2O_3$.		Found.			
			I.	II.	III.	IV.
C_{37}....	444	80·73	80·62	80·58	—	—
H_{30} ...	30	5·45	5·72	5·65	—	—
N_2....	28	5·09	—	—	5·24	5·30
O_3....	48	8·73	—	—	—	—
	550	100·00				

Analyses I and III were made with the prismatic crystals, II and IV with the needles.

The equation for the formation of the compound $C_{37}H_{30}N_2O_3$—which for reasons already stated we propose to name *cinnimabenzil*—is given on p. 464.

Action of Potash on Cinnimabenzil.—The finely-powdered compound was mixed with a 10 per cent. solution of caustic potash in methyl alcohol, and allowed to stand in a corked flask over night. The mixture became semi-solid, and on opening the flask a smell of ammonia was perceptible. Water was added, and the insoluble matter was filtered off. On acidifying the filtrate, it yielded only benzoic acid (identified by its melting point); but a faint cinnamon-like smell was perceptible during evaporation. The substance separated by filtration was shaken with ether; this removed a small quantity of a yellow gum, leaving the insoluble portion quite white. The substance thus obtained was practically insoluble in the ordinary organic solvents, but dissolved in hot phenol, and was precipitated from this solution as a crystalline powder on the addition of alcohol. By repeating this treatment three times, it was obtained with the constant melting point of 283°.

Analyses agreed with the formula $C_{30}H_{26}N_2O_2$:—

	Substance.	CO_2.	H_2O.
I........	0·1596	0·4691	0·0848
II........	0·1547	0·4547	0·0824

III. 0·1140 gram, burnt with copper oxide in a vacuum, gave 13·79 c.c. of dry nitrogen at 23·5° and under 339 mm. pressure. Nitric oxide was not present.

	Calculated for $C_{30}H_{26}N_2O_2$.		Found.		
			I.	II.	III.
C_{30}....	360	80·72	80·16	80·16	—
H_{26} ...	26	5·83	5·90	5·92	—
N_2....	28	6·28	—	—	6·24
O_2....	32	7·17	—	—	—
	446	100·00			

The substance contained a small quantity of ash which was weighed and deducted. The mode of formation of this compound has already been discussed (p. 464). In order to indicate its derivation from cinnimabenzil, we have named it *cinnidimabenzil*.

Action of Sulphuric Acid on Cinnimabenzil.—By boiling cinnimabenzil for a short time with dilute sulphuric acid (2 vols. of acid with 3 vols. of water), it is decomposed, yielding benzilimide, cinnamaldehyde, benzoic acid, and ammonia. Benzoic acid and benzilimide were identified by the melting point, the latter also by conversion into benzilam; the cinnamaldehyde was distilled with steam, and obtained as an oil with the characteristic odour. The reaction appears to take place according to the equation—

$$\underset{\text{Cinnimabenzil.}}{C_{37}H_{30}N_2O_3} + 2H_2O = \underset{\text{Benzilimide.}}{C_{21}H_{17}NO_2} + \underset{\text{Cinnamaldehyde.}}{C_9H_8O} + \underset{\text{Benzoic acid.}}{C_7H_6O_2} + NH_3.$$

The action of *concentrated* sulphuric acid on imabenzil (see following paper) corresponds with this, except that benzaldehyde is eliminated instead of cinnamaldehyde, and the benzilimide is converted by the concentrated acid into benzilam ($C_{21}H_{15}NO$). Both the mode of formation and the decomposition of cinnimabenzil, therefore, countenance the view that this compound is an imabenzil in which a benzaldehyde residue has been replaced by a cinnamaldehyde residue.

Various other reactions were tried with cinnimabenzil, but none of them yielded definite results.

Normal School of Science,
South Kensington.

XLVII.—*On Imabenzil.*

By FRANCIS R. JAPP, F.R.S., and W. PALMER WYNNE, B.Sc.

THE action of an alcoholic solution of ammonia on benzil was first studied by Laurent (*Revue Scientif.*, **10**, 122; **19**, 440; also *J. pr. Chem.*, **35**, 461), who obtained three compounds, to which he assigned the names and formulæ—

Imabenzil	$C_{14}H_{11}NO$,
Benzilimide	$C_{14}H_{11}NO$,
Benzilam	$C_{14}H_{9}N$.

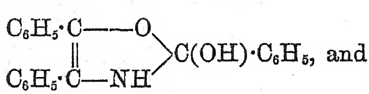
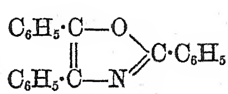
Working under somewhat different conditions, Zinin (*Annalen*, **34**, 190) prepared a compound which he named *azobenzil*, assigning to it the formula $C_{42}H_{30}N_2O_2$.

Henius (*Inaugural Dissertation*, Marburg, 1881), at Zincke's instance, undertook an experimental revision of the work already published on this subject. He came to the conclusion that Laurent's formulæ should be modified as follows:—

Imabenzil........	$C_{42}H_{32}N_2O_4$.
Benzilimide......	$C_{42}H_{32}N_2O_4$.
Benzilam........	$C_{42}H_{32}N_2O_2$;

and that Zinin's azobenzil was identical with benzilam. Henius's results were also communicated later in a note by Zincke (*Ber.*, **16**, 890).

One of us, in a further investigation of this subject (*Ber.*, **16**, 2636), has since shown that the formula of benzilam is $C_{21}H_{15}NO$, and that benzilimide, which yields benzilam by parting with the elements of water, is $C_{21}H_{17}NO_2$. Part of the benzil is first broken up, yielding benzaldehyde and benzoic acid (the latter in the form of benzamide or ethyl benzoate), and 1 mol. of nascent benzaldehyde then reacts with 1 mol. of benzil and 1 mol. of ammonia, forming either benzilimide or benzilam, according to the proportion of water eliminated in the reaction (*vide infra*). The following constitutional formulæ were assigned to these compounds:—


and


Benzilimide. Benzilam.

These formulæ have since been accepted by Henius (*Annalen*, **228**, 339).

But as regards the third compound, imabenzil, it was admitted (*Ber.*, **16**, 2640) that Henius's formula, $C_{42}H_{32}N_2O_4$, was probably correct. This opinion was, however, based upon an examination of *amorphous* imabenzil prepared by the method of Henius.

We have now prepared crystallised imabenzil, and find that it has the formula $C_{35}H_{28}N_2O_3$.

Henius prepares imabenzil by adding concentrated aqueous ammonia to a hot saturated alcoholic solution of benzil. A yellowish magma is the result, which, on the addition of more ammonia, becomes white. The whole is allowed to remain for an hour, after which the substance is collected on a filter and washed, first with water, then with alcohol, and finally with ether.

We find that imabenzil prepared by this method contains, mechanically enclosed, unaltered benzil, which the washing with alcohol and ether is quite incompetent to remove. This accounts for the low percentage of nitrogen which Henius found on analysis, and also for the large quantity of benzil which one of us described, in the communication already referred to, as obtained by boiling the above product with dilute sulphuric acid.

In order to obtain imabenzil, we employed the method described by Laurent. Benzil was dissolved in alcohol, so that the solution was saturated at 40°, and gaseous ammonia was passed into the warm solution to saturation. After standing for 24 hours, the liquid had deposited small colourless prismatic crystals of imabenzil. Sometimes needles of benzilimide separate along with the imabenzil, but this can be avoided by using a more dilute solution of benzil and allowing the ammoniacal liquid to stand longer, when well-developed crystals of imabenzil are obtained. Benzilimide and benzilam remain in the mother-liquor.

Henius asserts that imabenzil cannot be recrystallised without decomposition, and he therefore analysed the amorphous white powder obtained by his method. It is perfectly true that long boiling with alcohol decomposes even pure imabenzil, yielding among other products benzilimide; but by powdering the imabenzil first, boiling only for a short time with the alcohol, and filtering, a solution is obtained which, on standing, slowly deposits imabenzil in perfectly homogeneous crystals. By employing a solvent of lower boiling point, decomposition is avoided: the best result was obtained with methyl alcohol. A quantity of the crude crystallised imabenzil was finely powdered, and then boiled with a large quantity of methyl alcohol as long as any dissolved. The solution was filtered into a flask, in which it was allowed to stand for some days, in order to avoid evaporation during the crystallisation. Very lustrous crystals of imabenzil, from 3 to 4 mm. in diameter, were slowly deposited. Crystallised imabenzil

melts constantly at 194°, whereas Henius gives the melting point at 158—172°. We confirmed, however, Henius's statement that imabenzil heated at 140° for about an hour decomposes and melts.

The following results were obtained on analysis of the crystals deposited from ordinary alcohol :—

	Substance.	CO_2.	H_2O.
I.	0·1273	0·3728	0·0639
II.	0·1270	0·3725	0·0647

III. 0·1161 gram, burnt with copper oxide in a vacuum, gave 13·79 c.c. of dry nitrogen at 22·7°, and under 294·5 mm. pressure. Nitric oxide was not present.

IV. 0·1104 gram gave 13·79 c.c. dry nitrogen and nitric oxide at 22·5°, and under 282 mm. pressure, and after absorption of the nitric oxide, 13·79 c.c. dry nitrogen at 22·5°, and under 277 mm. pressure.

	Calculated for $C_{35}H_{28}N_2O_3$.		Found.			
			I.	II.	III.	IV.
C_{35}....	420	80·15	79·87	79·99	—	—
H_{28} ...	28	5·34	5·58	5·66	—	—
N_2....	28	5·34	—	—	5·34	5·33
O_3....	48	9·17	—	—	—	—
	524	100·00				

Analyses I, II, and III were made with one preparation; in IV a second preparation was employed.

The values for carbon and hydrogen agree with those obtained by Henius, whereas the nitrogen is nearly 1 per cent. higher in our analyses. This is accounted for by the fact that the impurity contained in imabenzil, prepared by Henius's method, is chiefly benzil, which contains C 80·00 and H 4·76 per cent. A quantity of benzil amply sufficient to lower the nitrogen to the extent observed in Henius's analyses might, therefore, be present without appreciably affecting the percentage of carbon and hydrogen.

As the point in dispute is therefore the percentage of nitrogen, we venture to call attention to the way in which our determinations were made. Following the method of Frankland and Armstrong, we burned the substance with oxide of copper in a Sprengel vacuum, and measured the nitrogen over mercury in a Frankland and Ward's gas-analysis apparatus, determining the quantity of nitric oxide (if any) present, and introducing this value into the calculation. A nitrogen determination made by this method is one of the most exact operations in the whole of analytical chemistry. A third deter-

mination of nitrogen in imabenzil, made with a different sample, and not included in the foregoing tabulated results, gave N 5·34 per cent.

We have to thank Mr. L. Fletcher for measurements of the crystals deposited from methyl alcohol. He reports thus:—

"*Imabenzil.*

Crystals, white.

Reach 3 or 4 millimetres in diameter.

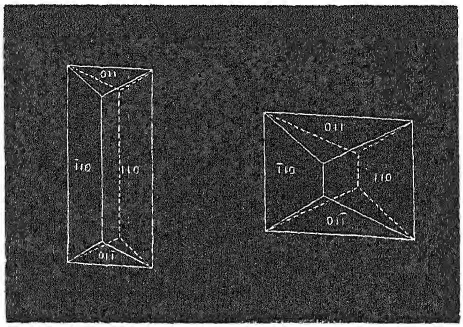


FIG. *a*. FIG. *b*.

. . . 'une poudre crystalline qui, examinée au microscope, ne doit offrir que des prismes droits à base rhombe, parfaitement nets, et dont les bases sont remplacées par deux facettes triangulaires qui reposent sur les arêtes verticales obtuses du prisme.'—*Laurent's description.*

This description applies exactly to the crystals prepared by Dr. Japp and Mr. Wynne (see Fig. *a**). Generally the prism is short as in Fig. *b*, and the crystals are then octahedrid in aspect.

Owing to the character of the faces, the following elements are only approximate :—

SYSTEM—Orthorhombic.

ELEMENTS—$a : b : c :: 1·525 : 1 : 0·788$,

or 011·010 = 51° 45′ : 101·001 = 27° 20′ : 110·100 = 56° 45′.

FORMS OBSERVED—{110}{011}.

Angles.	Observed.	Calculated.
110·$\bar{1}$10	66° 23′— 66° 41′	66° 30′
110·1$\bar{1}$0	113 14 —113 42	113 30
011·0$\bar{1}$1	78° 4′	76 30
011·01$\bar{1}$	103 8	103 30
011·110	58° 54′— 59° 22′	58 49
011·$\bar{1}$10	120 43 —121 12	121 11 "

* This figure also agrees with an approximate drawing given by Laurent.

The formation of imabenzil from benzil and ammonia may be expressed by the equation—

$$\underset{\text{Benzil.}}{3C_{14}H_{10}O_2} + 2NH_3 = \underset{\text{Imabenzil.}}{C_{35}H_{28}N_2O_3} + \underset{\text{Benzoic acid.}}{C_7H_6O_2} + H_2O,$$

the benzoic acid being eliminated in the form of ethyl benzoate or benzamide, substances which are always formed in the action of alcoholic ammonia on benzil.

The formation of the three compounds obtained from ammonia and benzil may therefore be explained by the assumption of the preliminary breaking up of a portion of the benzil, yielding benzoic acid (ethyl benzoate, benzamide) and benzaldehyde, and the condensation of the *nascent* benzaldehyde with benzil and ammonia according to the three equations :—

$$\text{I.}\quad \begin{array}{c} C_6H_5\cdot CO \\ | \\ C_6H_5\cdot CO \end{array} + C_6H_5\cdot CHO + NH_3 = \underset{\text{Benzilimide.}}{\begin{array}{l} C_6H_5\cdot C\text{——}O \\ \quad\;\, \| \qquad\quad \rangle C(OH)\cdot C_6H_5 \\ C_6H_5.C\text{—}NH \end{array}} + H_2O.$$

$$\text{II.}\quad \begin{array}{c} C_6H_5\cdot CO \\ | \\ C_6H_5\cdot CO \end{array} + C_6H_5\cdot CHO + NH_3 = \underset{\text{Benzilam.}}{\begin{array}{l} C_6H_5\cdot C\text{—}O \\ \quad\;\, \| \qquad \rangle C\cdot C_6H_5 \\ C_6H_5\cdot C\text{—}N \end{array}} + 2H_2O.$$

$$\text{III.}\quad 2\begin{array}{c} C_6H_5\cdot CO \\ | \\ C_6H_5\cdot CO \end{array} + C_6H_5\cdot CHO + 2NH_3 = \underset{\text{Imabenzil.}}{C_{35}H_{28}N_2O_3} + 2H_2O.$$

The last of these equations corresponds with that in which cinnamabenzil is formed from cinnamaldehyde, benzil, and ammonia (see preceding paper p. 464).

It is to be noted that *free* benzaldehyde with benzil and ammonia yields only lophine.

Action of Sulphuric Acid on Imabenzil.—The action of cold concentrated sulphuric acid on imabenzil was first studied by Laurent, who recommended this reaction as a means of preparing benzilam. Henius finds that benzilam and benzaldehyde are formed, together with a small quantity of benzil, but that if the solution of imabenzil is allowed to remain for some time, or is warmed before diluting, benzil is the chief product. We have repeated this experiment with crystallised imabenzil, but could not succeed in obtaining benzil, and we therefore conclude that this substance must have been contained as an impurity in the imabenzil employed by Henius. With crystallised imabenzil, we identified as the products of the reaction :

benzilam, benzaldehyde, benzoic acid, and ammonia. The reaction probably takes place according to the equation—

$$\underset{\text{Imabenzil.}}{C_{35}H_{28}N_2O_3} + H_2O = \underset{\text{Benzilam.}}{C_{21}H_{15}NO} + \underset{\text{Benz-aldehyde.}}{C_7H_6O} + \underset{\text{Benzoic acid.}}{C_7H_6O_2} + NH_3,$$

and corresponds with that in which cinnimabenzil is decomposed by boiling with dilute sulphuric acid (see preceding paper, p. 464), except that in the present case benzilam is formed instead of benzilimide, owing to the action of the concentrated acid.

But by boiling finely-powdered crystallised imabenzil with dilute sulphuric acid (1 vol. of acid to 2 vols. of water) for one hour, the imabenzil was converted into benzilimide and benzil; apparently in equal molecular proportions :—

$$\underset{\text{Imabenzil.}}{C_{35}H_{28}N_2O_3} + H_2O = \underset{\text{Benzilimide.}}{C_{21}H_{17}NO_2} + \underset{\text{Benzil.}}{C_{14}H_{10}O_2} + NH_3.$$

The proportion of benzilimide to benzil found was as 1·4 : 1, the theory demanding 1·5 : 1.

Boiling with glacial acetic acid also converted imabenzil into a mixture of benzil and benzilimide as described by Henius.

We are unable to suggest a constitutional formula for imabenzil.

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XLVIII.—*On the Action of Phosphoric Sulphide on Benzophenone.*

By Francis R. Japp, F.R.S., and Julius Raschen.

The action of the sulphides of phosphorus on ketones appears to have been but little investigated. Louguinine and Lippmann found that camphor, when heated with phosphoric sulphide, parts with the elements of water, yielding cymene. Wislicenus, by acting on acetone with phosphorous sulphide, obtained duplothiacetone $(C_3H_6S)_2$, and states that ethereal salts of phosphorous acid are formed at the same time.

We resolved to study the action of phosphoric sulphide on benzophenone. It seemed probable that in this case the action of the sulphide would be restricted to the carbonyl-group, and that we

should thus be attacking in its simplest form the problem of the action of this sulphide of phosphorus on a ketone. We find that two different compounds are formed, according to the temperature employed.

The action of phosphoric sulphide on a compound closely allied to benzophenone—benzhydrol—has however been studied by C. Engler, who in this way obtained a substance, $C_{26}H_{22}S_2$, melting at 151° (which he regarded either as a disulphide of the radicle $(C_6H_5)_2CH$–, or as a thiopinacone) together with an oily compound which he was unable to purify, but which formed a mercury compound agreeing in composition with that derivable from the thioalcohol $(C_6H_5)_2CH{\cdot}SH$. The compound, $C_{26}H_{22}S_2$, was also obtained by the action of potassium hydrosulphide or ammonium hydrosulphide on benzophenonidene dichloride, $(C_6H_5)_2CCl_2$.

Action of Phosphoric Sulphide at 100°.

Benzophenone was mixed with twice its weight of powdered phosphoric sulphide and heated for about 16 hours at 100°, shaking from time to time; the mass became green and afterwards blue. The product of the reaction was decomposed with water, and the insoluble residue was boiled with a large quantity of alcohol. The alcoholic solution deposited a greyish powder which was dissolved in a small quantity of benzene. By spontaneous evaporation, the benzene solution deposited large crystals of two kinds—colourless and yellow—which were separated mechanically. The yellow crystals proved to be sulphur. The colourless crystals, which became white and opaque on exposure to the air, were purified by recrystallisation, finally from alcohol, which deposited the substance in lustrous flat needles, melting at 152°. It agreed in its properties with the compound $C_{26}H_{22}S_2$ described by Engler. A sulphur determination (Carius) gave the following result:—

0·4505 gram substance gave 0·5469 gram barium sulphate.

	Calculated for $C_{26}H_{22}S_2$.	Found.
S in 100 parts............	16·08	16·57

It is deposited from benzene in two forms—either by spontaneous evaporation in large tabular crystals of monoclinic habit, which become opaque by exposure to the air or on heating to 100°, and probably contain benzene of crystallisation, or, by cooling of the hot saturated solution, in needles, which more closely resemble those from alcohol and do not become opaque.

Heated above its melting point to 200°, it turns deep blue.

Action of Phosphoric Sulphide at 140—150°.

A mixture of 50 grams of benzophenone with 100 grams powdered phosphoric sulphide was heated at 140° in an oil-bath until a thermometer placed in the mixture registered the temperature of the oil-bath. At first the temperature inside the flask rose to 150° owing to the heat given off in the reaction; as soon as the equalisation of temperature had taken place, the action was regarded as complete. The contents of the flask, which were of a deep blue colour, were boiled with water to decompose the excess of phosphoric sulphide, after which the insoluble matter was collected and boiled out twice with an excess of alcohol, washing with boiling alcohol on the filter. The greyish pulverulent residue was dissolved in boiling benzene, in which it was only sparingly soluble, and the filtered solution was mixed with twice its volume of light petroleum; this caused the separation of a white crystalline powder consisting of microscopic elongated plates. The substance was then recrystallised from boiling benzene, without the aid of petroleum, until it melted constantly at 226—227°. In melting, it decomposes, assuming a deep blue colour. It is practically insoluble in alcohol; hot benzene dissolves it sparingly, and on cooling deposits nearly the whole of the substance in the above-mentioned crystalline form.

In addition to carbon and hydrogen, it contained both phosphorus and sulphur. Analysis led to the formula $C_{26}H_{20}P_2S_5$:—

	Substance.	CO_2.	H_2O.
I........	0·3218	0·6669	0·1150
II........	0·2871	0·5923	0·0945

III. 0·8072 gram, oxidised by heating with sodium carbonate and mercuric oxide, gave 0·3119 gram of magnesium pyrophosphate.

IV. 0·5103 gram, oxidised with nitric acid, gave 0·2006 gram of magnesium pyrophosphate.

V. 0·5331 gram, oxidised by heating with sodium carbonate and mercuric oxide, gave 1·1526 grams of barium sulphate.

VI. 0·3956 gram, oxidised with nitric acid, gave 0·8488 gram of barium sulphate.

	Calculated for $C_{26}H_{20}P_2S_5$.		Found.					
			I.	II.	III.	IV.	V.	VI.
C_{26}..	312	56·32	56·52	56·26	—	—	—	—
H_{20}..	20	3·61	3·97	3·66	—	—	—	—
P_2 ..	62	11·19	—	—	10·79	10·97	—	—
S_5 ..	160	28·88	—	—	—	—	29·69	29·47
	554	100·00						

The substance is very hard to burn, and the full amount of carbon can only be obtained in analysis by mixing the substance with a large quantity of powdered lead chromate and heating very strongly.

When the compound is oxidised with a boiling solution of chromic anhydride in glacial acetic acid, benzophenone is regenerated. No substitution of sulphur or phosphorus in the phenyl-groups therefore takes place in the formation of this compound.

The formation of such a compound is most readily accounted for by supposing that thiobenzophenone is first formed by the replacement of oxygen in benzophenone by sulphur, and that 2 mols. of this compound then unite with 1 mol. of phosphorous sulphide (either contained in the phosphoric sulphide or, more probably, formed from it by abstraction of sulphur) to yield the new compound,

$$2CS(C_6H_5)_2 + P_2S_3 = C_{26}H_{20}P_2S_5.$$

The most probable formula for such a compound, formed by the union of 2 mols. of the sulphide of a dyad radicle, $C(C_6H_5)_2$ (which might be named *benzophenonidene*), with 1 mol. of the thianhydride, P_2S_5—and therefore presumably an ethereal thio-salt—would be—

$$\begin{array}{l} P{<}^{S}_{S}{>}C(C_6H_5)_2 \\ | \\ S \\ | \\ P{<}^{S}_{S}{>}C(C_6H_5)_2 \end{array}.$$

We propose to name this compound *benzophenonidene pyrothiophosphite.*

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XLIX.—*A Method for the Separation and Estimation of Zirconium.*

By G. H. Bailey, D.Sc., Ph.D., Assistant Lecturer in the Owens College.

It has already been pointed out (this vol., p. 149) that zirconium is completely precipitated from its solution in dilute sulphuric acid on addition of hydrogen peroxide alone. Hermann (*J. pr. Chem.*, **97**, 331), has described elaborate processes for the estimation of zirconium, but was unable to effect a satisfactory separation from titanium, iron, and some of the rarer earths. It was therefore desirable, in continu-

ance of the work referred to above, to ascertain whether the separation by means of hydrogen peroxide is capable of application in presence of varying amounts of such substances. Judging from Clève's results (*Bull. Soc. Chim.*, **43**, 53), there can be little doubt as to the similarity of thorium and zirconium in relation to this reagent, and where these two elements occur together they will in all probability both be precipitated on adding hydrogen peroxide to the solution; it is not proposed to consider the case of thorium in this place. Since, however, niobium and tantalum frequently accompany zirconium, the first has been included in the mixture. Solutions were made of the following composition:—

(1.)	Containing	0·02086	gram	ZrO_2	per cubic centimetre.
(2.)	,,	0·00417	,,	,,	,, ,,
(3.)	,,	0·00040	,,	TiO_2	,, ,,
(4.)	,,	0·00446	,,	,,	,, ,,
(5.)	,,	0·00071	,,	Nb_2O_5	,, ,,
(6.)	,,	0·00625	,,	Fe_2O_3	,, ,,

Hydrogen peroxide was added to a portion of each of these, and, except in the case of zirconium, no precipitation occurred even after several weeks. A mixture containing zirconia in larger quantity than the other constituents was made for determination from solutions 1, 3, 5, and 6. To the moderately acid solution, excess of hydrogen peroxide was added, and after standing in a stoppered flask 24 hours, the precipitated oxide was collected on a filter. It was perfectly white even after ignition, and weighed 0·4115 gram; no trace of iron or titanium could be detected in it. The filtrate was now diluted and boiled for 30 hours, the excess of the precipitating agent was thus decomposed, and a large part of the niobic and titanic oxides separated out. These were weighed together, the titanium being afterwards determined by Weller's colorimetric method and the niobium by difference. The filtrate from this still contained iron and some titanium, which were precipitated by means of ammonia. The results were—

	Taken.	Found.
ZrO_2..........	0·4105 gram	0·4115 gram.
Nb_2O_5	0·0103 ,,	0·0240 ,, (together with TiO_2)
TiO_2..........	0·0145 ,,	
Fe_2O_3	0·0950 ,,	0·0965 ,,

A second portion was taken containing relatively less zirconia and being altogether more dilute than the above, the solutions 2, 4, 5, and 6 being used. The precipitation and analysis were carried out exactly as in the previous case.

The results were—

	Taken.	Found.
ZrO_2..........	0·07188 gram	0·0745 gram
Nb_2O_5	0·01450 ,,	0·0718 ,,
TiO_2..........	0·05288 ,,	
Fe_2O_3	0·03887 ,,	0·0377 ,,

The general results being thus satisfactory, a third solution was made up with a view to testing the delicacy of the separation, as it is most important to be able to determine small quantities of zirconia in presence of a large excess of other oxides. The solution occupied 32 c.c. in bulk and contained—

ZrO_2	0·0065 gram.
TiO_2	0·1290 ,,
Fe_2O_3..........	0·1504 ,,

The precipitation of zirconia in this case was complete only after standing two or three days. The precipitate weighed 0·0055 gram and was free from iron and titanium. It was not considered necessary to determine the titanium and iron. As it is most desirable to have a simple and trustworthy method for the complete separation of zirconium from titanium and iron, further experiments were made in this direction.

Zirconia was precipitated by hydrogen peroxide in the presence of a very considerable excess of iron and of titanium respectively, the precipitate redissolved whilst still moist in dilute sulphuric acid, and the solution very carefully tested for these two elements. In no case was the zirconia found to contain either iron or titanium.

Properties of Zirconium Pentoxide.

The oxide described in my former paper is of course a hydrated oxide. In this form even when freshly precipitated it is insoluble in very dilute (1 per cent.) sulphuric acid or in dilute acetic acid, though on boiling for some time it partially dissolves, being probably first decomposed.

The ordinary hydrated dioxide on the other hand, especially in the freshly precipitated condition, is readily dissolved by these acids, and indeed a separation of the two oxides can be made by treating a mixture of the two with such acid. Oxalic acid dissolves both oxides quite readily, and the fact may here be emphasised that zirconia in the moist state dissolves in this acid; for although Berlin (*J. pr. Chem.*, 58, 147) has already pointed this out, the contrary is stated to be the case in a large number of authoritative text-books. In dilute

acetic acid, the pentoxide is quite insoluble, and it was therefore not unlikely that the precipitation might be more advantageously carried out in this medium than in the presence of mineral acids. A repetition of Haas' work (*Ber.*, **17**, 2249) on the peroxides of cadmium, substituting the acetate for the sulphate, showed that whereas the latter gives an oxide of the composition Cd_3O_5, the former gives not the faintest trace of peroxide. In the case of zirconium, however, the oxide obtained by precipitation in an acetic acid solution proved to be the pentoxide and gave the ratio—

$$ZrO_2 : O :: 122 : 7{\cdot}3,$$

the calculated relation for the pentoxide being—

$$ZrO_2 : O :: 122 : 8.$$

A portion of the pentoxide was now taken and dried at 100°, and the oxygen determined by the iodometric method, the zirconia by heating a separate portion over the blowpipe until the weight was constant. The water of hydration was obtained by difference.

The results were—

ZrO_2	75·51	—
O	3·87	3·76
H_2O	20·62	—
	100·00	

Portions dried at 15° over sulphuric acid gave—

ZrO_2	76·81	74·61	75·66
O	—	2·44	3·13
H_2O	—	22·95	21·21

The oxide seems therefore to have the composition $Zr_2O_5,4H_2O$, though in the dry state it is not of constant composition, and loses at ordinary temperature about one-fifth of its peroxide oxygen, and at 100° about one-half.

Clève has (*loc. cit.*) described an oxide containing more oxygen than the foregoing, which he obtained by adding ammonia and hydrogen peroxide to a salt of zirconium.

Although hitherto the several specimens of peroxide, which I have prepared, had invariably proved to be the pentoxide, I have recently obtained the higher oxide, and this also on addition of hydrogen peroxide alone.

What the conditions are under which this higher oxide is produced I am not prepared to say. I obtained it by treating the solution of the sulphate (prepared by heating the double fluoride of potassium and zirconium with sulphuric acid) *immediately* with hydrogen

peroxide before the basic potassium salt had had time to separate. In previous preparations, the solution had been allowed to stand and was filtered before adding the peroxide; it was therefore more dilute. This higher oxide is no doubt the compound described by Clève, and has the composition ZrO_3.

In its properties, it resembles the pentoxide, behaving in the same way towards acids.

It seems, however, to be more stable, and can be dried at ordinary temperatures without undergoing decomposition. This is shown in the following experiments. The oxide was freed from moisture by placing it in a stream of air dried over caustic potash and sulphuric acid. Portions were then analysed in the same manner as the pentoxide, and the results obtained gave the following percentage composition:—

ZrO_2	52·17	51·84	—
O	—	7·01	6·85
H_2O	—	41·15	—

This answers fairly well to the composition $ZrO_3,5H_2O$. Dried at 100°, it gave—

ZrO_2	59·61	59·17
O	—	3·41
H_2O	—	37·42

At this temperature, therefore, it loses about 1 mol. H_2O and half its additional oxygen. The water of hydration cannot be looked on as perfectly definite in amount. Calculating for the anhydrous oxides we have the following numbers:—

	ZrO_2.	O.
Dried at 15°	88·13	11·91
,, ...	—	11·64
,, 100°	94·55	5·45
Calculated for ZrO_3 ..	88·41	11·59

and for the pentoxide:—

	ZrO_2.	O.
Dried at 15°	96·32	3·68
,, 100°	95·07	4·93
Calculated for Zr_2O_5..	93·85	6·15

Note.—In a private communication with which I have been favoured by Prof. Clève, he suggests that these peroxides may possibly contain traces of sulphuric acid, but on examination I can obtain no evidence of such contamination.

L.—*Derivatives of Taurine.* Part II.

By J. WILLIAM JAMES, Ph.D., F.C.S., University College of South Wales, Cardiff.

THE preparation of trimethyltaurine by the action of a concentrated alcoholic solution of trimethylamine on the corresponding salt of β-chlorethylsulphonic acid has been already described (Trans., 1885, 372). I have since then made larger quantities of this substance, and carried out a few experiments with a view to determine whether trimethyltaurine is to be regarded as the methyl ether of dimethyltaurine, $C_2H_4<^{NMe_2}_{SO_2 \cdot OMe}$, as is warranted by its synthetical formation, or as a compound containing pentad nitrogen, $C_2H_4<^{NMe_3}_{-SO_2-}>O$, analogous to trimethylglycocine, $C_2H_4<^{NMe_3}_{-CO_2-}>O$ (betaïne).

Decomposition of Trimethyltaurine with Alkalis.

15 grams of pure trimethyltaurine were dissolved in water, 20 grams of crystallised barium hydroxide added, and the mixture boiled in a flask until the steam was neutral to litmus-paper. The evolved gases were passed through a well-cooled **U**-tube containing dilute hydrochloric acid. This solution was afterwards distilled very carefully to one-third, the distillate twice distilled to one-third, potassium carbonate added, and again distilled; on testing this last distillate for methyl alcohol, no trace of it could be detected. A portion of the hydrochloric acid solution was then precipitated with platinum tetrachloride in three equal portions, and the dried platinochloride analysed with the following results:—

Fraction I. 1. 0·2474 gram substance, after ignition, yields 0·0909 gram platinum.

2. 0·3272 gram substance, after ignition, yields 0·1204 gram platinum.

Fraction II. 0·2141 gram substance, after ignition, yields 0·0790 gram platinum.

Fraction III. 0·243 gram substance, after ignition, yields 0·089 gram platinum.

	Calc. for trimethylammonium platinochloride, $2N(CH_3)_3HCl,PtCl_4$.	Found. Fraction. I.	II.	III.
Pt.	36·81 p. c.	1. 36·74	36·89	36·62
		2. 36·79	—	—

These numbers leave no doubt that the gas evolved in the decomposition of trimethyltaurine is nothing but pure trimethylamine.

The residue in the flask containing the barium was heated to boiling with addition of more water, and then poured into a hot aqueous solution of 6·28 grams of concentrated sulphuric acid to remove the barium. After filtering off the barium sulphate, the strongly acid liquid was evaporated to a syrup on the water-bath, diluted with water, neutralised with potassium carbonate, and evaporated to dryness. The residue of crude potassium salt was well ground up with strong alcohol and digested with it for some time; on filtering the solution, silky needles were soon deposited which resembled potassium isethionate both in appearance and in being sparingly soluble in alcohol. The substance after recrystallisation was dried at 100°, and a complete analysis has shown that it consisted of the above salt in a state of purity.

I. 0·2054 gram substance burnt with $CuO,PbCrO_4$ and Cu gave 0·0590 gram H_2O and 0·1065 gram CO_2.

II. 0·205 gram substance fused with KHO and KNO_3 produced 0·3006 gram $BaSO_4$.

III. 0·1786 gram substance produced 0·095 gram K_2SO_4.

	Calculated for potassium isethionate, $OH{\cdot}C_2H_4{\cdot}SO_3K$.		Found. I.	II.	III.
C_2	24	14·63	14·14	—	—
H_5	5	3·05	3·19	—	—
S	32	19·51	—	20·13	—
O	64	39·03	—	—	—
K	39	23·78	—	—	23·84
	164	100·00			

From the above experiment it follows that trimethyltaurine when boiled with excess of alkali decomposes, according to the equation—

$$C_2H_4{<}^{NMe_3}_{-SO_2}{>}O + H_2O = NMe_3 + OH{\cdot}C_2H_4{\cdot}SO_3H,$$

into trimethylamine and isethionic acid.

Cyanamide and Trimethyltaurine.

1·5 gram of trimethyltaurine and 0·37 gram cyanamide were allowed to stand in concentrated aqueous solution for some days, but no action took place: the mixture was afterwards heated in a sealed tube for four hours at 120°; on evaporating the liquid, a crystalline substance separated, insoluble in alcohol, and having a sweet taste:

an estimation of the nitrogen proved it to be unaltered trimethyltaurine.

0·1616 gram substance produced 12·3 c.c. moist nitrogen at 15° and 757·7 mm.

	Calculated for trimethyltaurine.	Found.
N	8·4	8·73

Hydriodic Acid and Trimethyltaurine.

So far as is known, compounds containing a methoxyl-group are decomposed by boiling with hydriodic acid, sp. gr. 1·68, with formation of methyl iodide, and the number of methoxyl-groups can be easily estimated by converting the methyl iodide into silver iodide as described in a recent paper by Zeisel (*Monats. Chem.*, **6**, 989; Abstr., 1886, 493). An experiment carried out precisely as described in this memoir gave no trace of methyl iodide after boiling for an hour; this appears to me to exclude the formula $NMe_2{\cdot}C_2H_4{\cdot}SO_2{\cdot}OMe$ (Trans., 1885, 367), as such a compound would undoubtedly yield methyl iodide under this treatment.

On heating trimethyltaurine with hydriodic acid in a sealed tube at 200°, a reaction takes place with separation of iodine; a strong odour of mercaptan compounds is produced, but no methyl iodide even under these circumstances could be detected.

Constitution of Taurine and its Alkyl-derivatives.

The ease with which trimethyltaurine is decomposed by alkalis into trimethylamine and isethionic acid seems to show conclusively that it must have a constitution very different from taurine and its derivatives with monamines and diamines, for had these compounds a similar constitution there is no reason why they should not also be decomposed by boiling with alkalis into monamines and diamines and isethionic acid, but it has already been shown that such is not the case (Trans., 1885, 368).

Again, the acid reaction of taurine, mono- and di-substituted taurines, and their behaviour with cyanamide strongly supports the above supposition, as all these substances unite with it forming well characterised crystalline compounds (Engel, *Ber.*, 8, 1597; Dittrich, *J. pr. Chem.* [2], **18**; James, Trans., 1885, 373). Trimethyltaurine, on the other hand, is neutral to litmus, and forms no combination with cyanamide under similar conditions.

It follows then that trimethyltaurine is to be represented as a saturated compound containing pentad nitrogen and analogous to

trimethylglycocine (betaïne), whereas taurine and mono- and di-substituted taurines containing triad nitrogen are capable of combining with a molecule of cyanamide. The following general formulæ for taurine and its alkyl-derivatives,

Taurine.	Monalkyltaurine.	Dialkyltaurine.	Trialkyltaurine.
$C_2H_4<{NH_2 \atop SO_2{\cdot}OH}$	$C_2H_4<{NHR' \atop SO_2{\cdot}OH}$	$C_2H_4<{NR'_2 \atop SO_2{\cdot}OH}$	$C_2H_4<{NR'_3 \atop SO_2-}>O$,

would then be in accordance with the experimental evidence, and a trialkyl taurine, as a compound containing pentad nitrogen, would presumably decompose more or less readily into two molecules, which has been shown to be true of the trimethyl-derivative.

Action of Ammonia on β-Chlorethylsulphonic Chloride, $Cl{\cdot}C_2H_4{\cdot}SO_2Cl$.

Some time ago I investigated this reaction with the intention of preparing the amide of β-chlorethylsulphonic acid, but only succeeded in obtaining an oily substance free from chlorine (Trans., 1883, 47), and in such small quantities that I was unable at the time to study it further. Working now with larger quantities of pure β-chlorethylsulphonic chloride, I have obtained satisfactory results. 30 grams of the chloride were dissolved in 300 c.c. of absolute ether and dry ammonia gas passed in to thorough saturation, the flask being well cooled during the experiment. The precipitate which had formed was collected, dried over sulphuric acid, and analysed.

I. 0·398 gram substance burnt with CuO, $PbCrO_4$, and Cu gave 0·2265 gram H_2O and 0·1852 gram CO_2.

II. 0·2454 gram substance burnt with CuO and copper gauze with sodium hydrogen carbonate, produced 44 c.c. of moist nitrogen at 19° C. and 767 mm.

III. 0·581 gram substance dissolved in water and acidified with nitric acid, produced 0·775 gram AgCl.

IV. 0·528 gram substance treated similarly gave 0·7025 gram AgCl.

	Calculated for $NH_2{\cdot}C_2H_4{\cdot}SO_2NH_2$ + $2NH_4Cl$.	Calculated for $C_2H_4<{NH \atop SO_2}$ (ring) + $2NH_4Cl$.	Found. I.	II.	III.	IV.
C....	10·39	11·21	12·69	—	—	—
H ...	6·92	6·07	6·32	—	—	—
N ...	24·24	19·62	—	20·36	—	—
Cl...	30·73	33·17	—	—	32·99	32·89
S....	13·85	14·95	—	—	—	—
O ...	13·87	14·98	—	—	—	—
	100·00	100·00				

From these numbers, it is clear that the precipitate consisted of a mixture of a substance of the formula $C_2H_5NSO_2$ with ammonium chloride: this is specially apparent from the nitrogen and chlorine determinations. Its formation is expressed by the following simple equation: $Cl{\cdot}C_2H_4{\cdot}SO_2Cl + 3NH_3 = 2NH_4Cl + C_2H_4\langle{NH \atop SO_2}\rangle$,

unless indeed the compound, $NH_2{\cdot}C_2H_4{\cdot}SO_2NH_2$ (the amide of taurine, $NH_2{\cdot}C_2H_4{\cdot}SO_2OH$), is so unstable that it decomposes on standing over sulphuric acid in the cold, which seems hardly probable.

The ammonium chloride was easily removed from this precipitate by adding silver oxide in slight excess, evaporating the mixture to dryness on the water-bath, taking up with water, and filtering off the silver chloride. The filtrate was found to still contain a small quantity of silver which was got rid of by hydrogen sulphide; on evaporating the liquid, now free from silver, to dryness, and drying at 100°, the new substance was obtained as a yellowish oil which, on cooling, set to a hard mass resembling gum arabic.

An analysis (I and II) gave the following numbers, and they agree as well as can be expected with *ethanesulphonimide*, $C_2H_4\langle{NH \atop SO_2}\rangle$ (anhydrotaurine). The other nitrogen determinations (III, IV, and V) were made from separately prepared samples.

I. 0·4604 gram substance burnt with CuO, $PbCrO_4$, and Cu produced 0·2312 gram H_2O and 0·359 gram CO_2.

II. 0·3562 gram substance burnt with CuO and copper gauze with sodium hydrogen carbonate, gave 43 c.c. moist nitrogen at 10° and 763 mm.

III. 0·178 gram substance similarly treated gave 21 c.c. moist nitrogen at 16° and 765 mm.

IV. 0·147 gram substance by the soda-lime method yielded 0·137 gram platinum.

V. 0·113 gram substance by the soda-lime method yielded 0·110 gram platinum.

Calculated for ethanesulphonimide. $C_2H_4\langle{NH \atop SO_2}\rangle$.			Found.				
			I.	II.	III.	IV.	V.
C_2	24	22·43	21·26	—	—	—	—
H_5	5	4·67	5·57	—	—	—	—
N	14	13·06	—	14·34	13·60	12·9	13·7
S......	32	29·92	—	—	—	—	—
O_2	32	29·92	—	—	—	—	—
	107	100·00					

Ethanesulphonimide is a solid resembling gum arabic in appearance: it melts between 45° and 50°, and at 100° becomes more or less mobile. It has a bitter taste. In cold water, it is scarcely soluble, but mixes with hot water in all proportions: it is insoluble in alcohol or ether.

No taurine was formed on heating it with water alone in a sealed tube at 150°, neither did the addition of a drop of hydrochloric acid bring about a reaction. No compound with hydrochloric acid and platinum tetrachloride could be obtained. It is not decomposed by boiling with barium hydroxide, and this may be taken advantage of for obtaining this substance from its admixture with ammonium chloride, the barium being subsequently removed by sulphuric acid.

Metallic Derivatives of Ethanesulphonimide.

If freshly precipitated mercuric oxide is gradually added to a hot concentrated aqueous solution of ethanesulphonimide, it is dissolved, and on filtering the liquid, after a slight excess of the oxide has been added, the mercury compound separates on cooling as an amorphous white precipitate which aggregates into several semi-solid globules on standing. The precipitate was washed once or twice with distilled water and dried over sulphuric acid.

I have not been able to prepare this mercury compound in a state of purity, it is always mixed with more or less of the original substance, probably carried down with it mechanically, but the following numbers obtained on the analysis of a sample can leave no doubt but that the hydrogen of the imide-group has been replaced by mercury—two molecules of imide being required for one molecule of mercuric oxide—

$$2C_2H_4\left<\begin{matrix}NH\\|\\SO_2\end{matrix}\right. + HgO = \left[C_2H_4\left<\begin{matrix}N\\|\\SO_2\end{matrix}\right.\right]_2 Hg + H_2O.$$

I. 0·2300 gram substance burnt with CuO and copper gauze produced 15·6 c.c. moist nitrogen at 13° and 757 mm. = 7·86 per cent. N.

II. 0·1185 gram substance dissolved in hydrochloric acid with addition of a drop of nitric acid, gave 0·0548 gram HgS = 0·04724 gram Hg = 39·86 per cent.

If the excess of nitrogen over that required by the formula of the mercury compound be calculated to ethanesulphonimide and subtracted, the percentage of mercury is as near as possible the theoretical.

0·1185 − 0·0213 (admixture of imide calculated from excess of N) = 0·0972 gram pure mercury compound.

	Calculated for $(C_2H_4NSO_2)_2Hg$.	Found.
Hg	48·54	48·60

Silver oxide is also dissolved by the aqueous solution of ethanesulphonimide, and doubtless forms a compound analogous to the above.

In the *Berichte*, **18**, 869, Leymann describes experiments with β-chlorethylsulphonic chloride and aniline: he obtained three substances in this reaction—

$$Cl{\cdot}C_2H_4{\cdot}SO_2NHPh;\ NHPh{\cdot}C_2H_4{\cdot}SO_2NHPh;\ \text{and}\ C_2H_4\left\langle\begin{matrix}NPh\\ |\\ SO_2\end{matrix}\right. .$$

I have found no indication of any analogues of the two first compounds, but this ethanesulphonimide is the compound corresponding to the latter substance, which Leymann has named *anhydrophenyltaurine*. It is true such a compound and water should yield phenyltaurine or phenyltaurine on hydrolysis, but there is no evidence to support these assumptions, and I have in vain endeavoured to prepare taurine from ethanesulphonimide by heating it with water and dilute acid under pressure. The name *anhydro* is therefore misleading and should be discontinued in connection with this new class of substances, for they are neither acids or anhydrides, but simply analogous to the imides of the fatty series with carboxyl. Leymann's body should be called phenylethanesulphonimide, and the relation between taurine and ethanesulphonimide is plainly seen from the following formulæ :—

$NH_2{\cdot}C_2H_4{\cdot}SO_2{\cdot}OH$, amidoethanesulphonic acid (taurine).
$NH_2{\cdot}C_2H_4{\cdot}SO_2NH_2$, amidoethanesulphonamide (unknown).

$$C_2H_4\left\langle\begin{matrix}NH\\ |\\ SO_2\end{matrix}\right. ,\ \text{ethanesulphonimide.}$$

LI.—*The Influence of Remelting on the Properties of Cast Iron. Notes on Sir W. Fairbairn's* 1853 *Experiments.*

By Thomas Turner, Assoc. R.S.M., Demonstrator of Chemistry, Mason College, Birmingham.

In a recent paper, published in the Journal of this Society (Trans., 1886, p. 130), I have entered at some length into a consideration of the experiments conducted by Sir William Fairbairn to ascertain the effect of repeated remelting on the properties of cast iron (*B. A. Report*, 1853, p. 87). I endeavoured to show "that the effect attributed to remelting may be sufficiently explained by a consideration of the chemical changes which took place." These changes I then believed to be a gradual increase of silicon (owing to the metal being melted in a cupola in contact with fuel), accompanied by the fact "that sulphur considerably increased about the fourteenth and fifteenth melting, rendering the metal hard, white, and brittle."

In the discussion which followed the reading of that paper, it was stated by Professor Unwin, who assisted in these experiments, that remelting was not conducted in a cupola, as I had been led to suppose in the first place, but that an air-furnace was used for this purpose. Since then a fortunate opportunity has been presented to me for the examination of what are probably the only specimens of these test bars now in existence. The result of this examination has been to considerably modify my original conclusions as to the details of the changes, though it has amply confirmed my contention that the effects observed could be sufficiently explained by a consideration of the changes in chemical composition.

My former conclusions were based upon the following analyses, which were given in the original paper on the authority of Professor Calvert:—

	Percentage of		
No. of meltings.	Si.	S.	C.
1	0·77	0·42	2·76
8	1·75	0·60	2·30
10	1·98	0·26	3·50
18	2·22	0·75	3·75

It will be shown later that these analyses are altogether erroneous, and at present I am not able to make out any connection whatever

between the numbers given above and the actual composition of the specimens.

For the specimens I have been able to examine, I am indebted to the kindness of Professor Unwin, and I would here record my deep indebtedness to him for resigning into my hands, for the purpose of chemical analysis, specimens which he highly prized, and which are of special value as the only remains of the experiments of 33 years ago. It may be well to mention here that the identity of these pieces is thoroughly assured. In forwarding them Professor Unwin said, "There is absolutely no doubt that the pieces sent you were broken off Fairbairn's remelted bars. I have preserved absolutely no other specimens of cast iron, so there has been no mixing of two sets. The only possible doubt is as to the numbering."

As a doubt might be possible in the latter respect, a short account may be given of the pieces received. Of these there were seven in all, each being 1 inch square in section, as described in the original paper. The largest piece was about 1 inch in length also. Five of the specimens were numbered (Nos. 1, 8, 14, 15, 18), the labels being gummed on, and having been attached over 25 years ago. In each case the character of the metal exactly agreed in hardness and appearance with the description given in the original paper, which contains a minute account of the fractures. In two of these pieces, Nos. 15 and 18, we have a further confirmation in the sketches given in the paper, which exactly correspond with the metal examined. In one case a specimen was not numbered. Its appearance was very characteristic, white on the outside, but with a small circle of grey inside about three-eighths of an inch in diameter. This appearance was sketched in the original memoir, and made it certain that the piece was from the sixteenth melting. In one case, the label had become quite illegible. As there was a considerable amount of iron rust on this label, it was not possible to restore the ink marks by ordinary processes. The label was therefore carefully detached and held up to the light. The figure 1 was plainly seen, and part of a second figure could also be discerned. From its shape and other circumstances this could be only either a 2 or a 3, and the evidence appeared to be strongly in favour of 12 as the right number. Professor Unwin said of it, "I have a strong suspicion that this is the bar of maximum transverse strength (12th), but of course I have no proof. I think it is almost certain I should have retained a specimen of that bar." In hardness it was intermediate between 8 and 14, and its composition also favoured this view, so that the identity of this specimen may be considered assured.

The chemical examination was rendered more than usually difficult, owing to the comparatively small quantity of material to be operated

upon, and the necessity for the preservation of a portion of each piece for reference at any future time.* In one case also (the 18th melting), the specimen was so hard that it could not be touched by a file or drill, and a sample for analysis could only have been obtained at great risk to the specimen itself. As Professor Unwin prized this particular piece more highly than several of the others, and as the analyses already made rendered the action quite evident, it was not considered well to proceed further than an estimation of combined carbon in this case. When it was found that my analyses gave results so very different from those of Professor Calvert, I thought it well to forward my results, so far as they had then gone, to Professor Unwin, suggesting that samples should be sent to some independent chemist of known experience in iron analyses. As a result, a small quantity of borings from each bar was forwarded to Mr. J. P. Walton, Assoc. R.S.M., of the Wishaw Iron Works, and his analyses afford strong confirmation to my own conclusions. In some cases, especially with manganese and phosphorus, the agreement is not so good as might be desired, though in each case the general direction of the change is correctly indicated. But in forwarding his results Mr. Walton said, "I am sorry that the quantity of material does not allow of my ordinary processes being followed in every case." The same remark would apply to my own analyses; for if the supply of material had been more abundant the details of the operations would have been modified in several instances.

The methods adopted in my analyses were as follows. Of each sample, two quantities, each of 2 grams, were dissolved in aqua regia, and evaporated to dryness on the water-bath. After heating at 100° for some time, the residue was extracted with a little hydrochloric acid and the silica separated and weighed. To the filtrate a little barium chloride was added, the solution nearly neutralised, and allowed to stand at least 24 hours. After filtering off the barium sulphate, the solution was treated in one case for manganese and in the other for phosphorus. The first was separated by means of ammonium carbonate, and precipitated by bromine in concentrated solution, alkaline with ammonia. The phosphorus was weighed as pyrophosphate of magnesia after precipitation as molybdate. The total carbon was determined by combustion, according to the method I have described (*Birmingham Philosophical Society's Proceedings*, vol. iv, Part II, p. 404; incorrectly abstracted, Abstr., **48**, 1161), while, to save material, the combined carbon was estimated colorimetrically. Of these methods, it should be observed that the phosphorus is probably rather low, owing to details in the methods

* At least half of each of the specimens Nos. 8, 12, 14, 15, 16, and 18 have been returned to Professor Unwin. These pieces may be useful for future reference.

employed, while the values for combined carbon show the direction of the change rather than the actual amount of this constituent. The results are given in Table A.

TABLE A.—*Analyses by T. Turner.*

No. of melting.	Total carbon.	Combined.	Silicon.	Sulphur.	Manganese.	Phosphorus.
1........	2·67	0·25	4·24 4·19	0·04 0·02	1·81 1·74	0·40
8	2·97	0·08	3·27 3·20	0·05 0·04	0·55	0·48
12........	2·94	0·85	2·55 2·53	0·10 0·11	0·23	0·50
14........	2·98	1·31	2·17 2·14	0·13 0·14	0·17	0·53
15........	2·87	1·75	1·95 1·96	0·14 0·15	0·15	0·56
16........	2·88	*	1·88 1·96	0·20 0·22	0·14	0·61
18........	—	2·20				

The methods adopted by Mr. Walton for the determination of sulphur and silicon were almost identical with my own. The phosphorus was weighed as molybdate. The results are given in Table B.

TABLE B.—*Analyses by J. P. Walton.*

No. of melting.	Silicon.	Sulphur.	Manganese.	Phosphorus.
1............	4·22	0·03	1·32	0·53
8............	3·15	0·06	0·61	0·58
12............	2·47	0·13	0·45	0·60
14............	2·24	0·12	0·29	0·57
15............	1·93	0·18	0·19	0·59
16............	1·80	0·17	0·10	0·61

It will be seen that Mr. Walton's determinations of silicon and sulphur agree very fairly with my own. In phosphorus, the agreement is not so good, the difference in the eighth and twelfth meltings being 0·1 per cent. However, these differences are not such as to

* Varied in parts; outside white, inside grey.

materially affect the iron, and their cause has already been partly indicated. The most serious divergence is seen in the first melting, where a difference of 0·5 per cent. of manganese and 0·13 per cent. of phosphorus occurs. In this case the whole of the specimen was used in the analysis, so we were unable to check the result in duplicate as was intended. It must be remembered, however, that owing to the small quantity of material at our disposal the precipitates of manganese generally weighed but a few milligrams, so that if the results agree in showing the direction in which the change took place, it is perhaps as much as can be reasonably anticipated.

From these analyses, I have endeavoured to deduce the probable composition of the specimens examined. In most cases, the numbers are the mean of those previously given; but in a very few instances when any considerable difference was observed, I have ventured to attach rather more importance to a particular determination which appeared most trustworthy. The results are given in Table C.

TABLE C.—*Composition of Test Bars.*

No. of melting.	Total carbon.	Combined.	Silicon.	Sulphur.	Manganese.	Phosphorus.
1........	2·67	0·25	4·22	0·03	1·75	0·47
8........	2·97	0·08	3·21	0·05	0·58	0·53
12........	2·94	0·85	2·52	0·11	0·33	0·55
14........	2·98	1·31	2·18	0·13	0·23	0·56
15........	2·87	1·75	1·95	0·16	0·17	0·58
16........	2·88	—	1·88	0·20	0·12	0·61
18........	—	2·20				

It will be found on comparing these results with those previously given by Calvert, that with the solitary exception of the total carbon in the first melting, our conclusions are entirely at variance. In particular, it will be seen that the silicon, on the numbers for which my previous conclusions depended, varies in an exactly opposite direction, and over a very different range to that which was previously supposed.

It may be mentioned, however, that doubts have been cast on the accuracy of Calvert's analyses by several writers of experience on this subject, though they had not the opportunity of examining the specimens. Thus Snelus, writing over 15 years since, in the first volume of the *Journal of the Iron and Steel Institute* (p. 37), when speaking of the results observed in Fairbairn's experiments, said he believed the explanation to be, "that at each successive melting the silicon, and perhaps to a slight extent the carbon, decreases; but the iron gradually takes up sulphur and phosphorus from the fuel, and

the deterioration due to these elements more than counterbalances the increased strength due to diminished carbon and silicon." In *Chemistry Applied to the Arts and Manufactures*, 8, 861, when discussing the effects of remelting iron in a cupola, the above opinion of Snelus is put forward, and the remark made, "The chemical analyses of some of these samples, which were made by Calvert, do not appear to support these conclusions. The analytical results, however, as will be seen from an examination of the figures, are so remarkable that it is evident they are *not reliable*, and it is desirable that they should be repeated." It may also be remarked that other analyses published by Calvert at the same period (*Inst. C.E.*, 1852—53, 354) show that Eglinton iron was rather highly siliceous, containing 3·12 per cent. of silicon, while in the present instance it is returned with only 0·77 per cent.

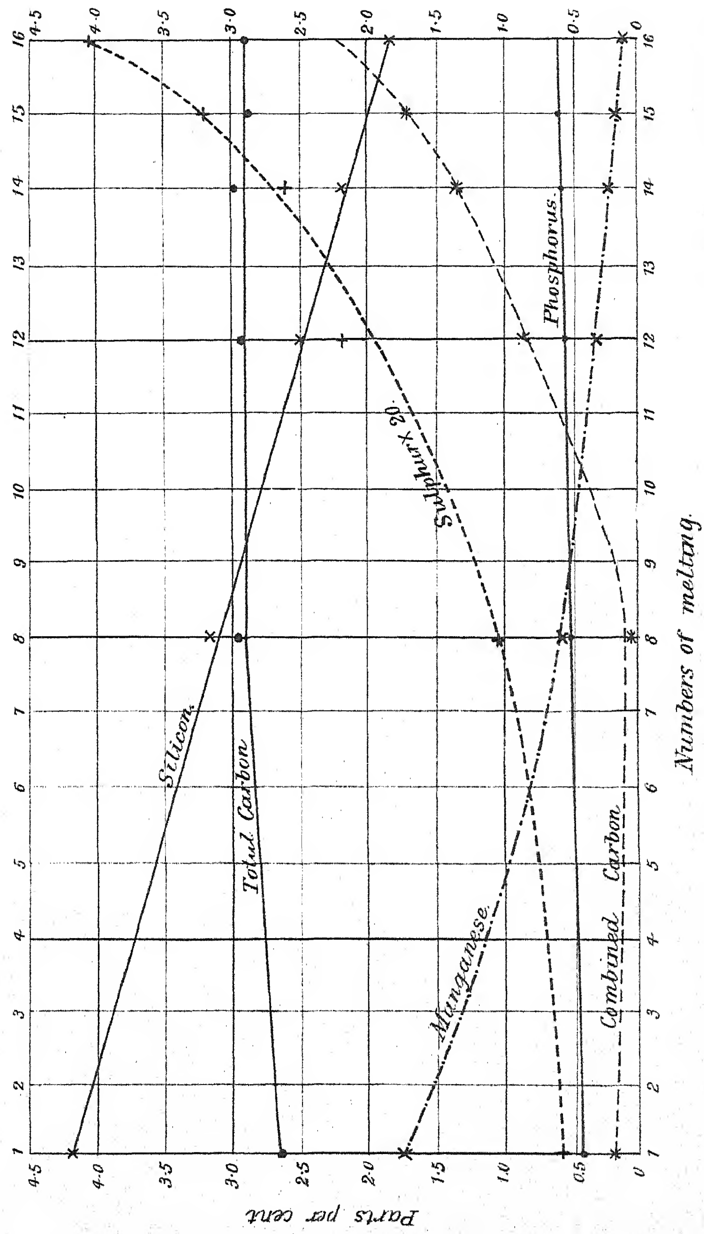
It will be seen that, like myself, Snelus was of opinion that remelting had been performed in a cupola. But, in spite of this slight misunderstanding, the correctness of his explanation is very remarkable. In my former paper, depending on Calvert's analyses, I have endeavoured to account for the effect observed as due to a gradual increase of silicon, combined with a considerable absorption of sulphur in the later meltings. My failure to detect Calvert's error in the proportion of silicon was due, in part at least, to a lack of knowledge of the influence of definite quantities of each of the other elements present. This knowledge I have endeavoured to render more systematic in my last paper, "On the Constituents of Cast Iron," recently read before the Iron and Steel Institute. A comparison of the values given in that paper with Calvert's analysis of the first melting, will show that his results are quite untrustworthy, since his values are those which are characteristic of a *white* iron, while the metal operated on was a soft grey.

The action during remelting in a reverberatory furnace is essentially oxidising, and it is therefore natural to expect that the chemical changes would be the same during remelting as during "refining," puddling, and the open hearth or Bessemer process. This expectation is realised on examining Table C, the only point of difference being found in the gradual increase of sulphur.

In Fig. 1 the chemical changes produced during remelting are represented by curves. These closely correspond in general character with those given by Windsor Richards, and other authorities, for the early part of a Bessemer blow. The exception, to which I have previously referred, noticed in the case of sulphur, is a little obscure in origin, though the fact is undoubted. The effect of this is of the utmost importance, and to make it more visible the scale used for sulphur is 20 times that used for the other elements.

Fig. I.

INFLUENCE OF RE-MELTING ON THE PROPERTIES OF CAST IRON.



HARRISON & SONS LITH. ST MARTINS LANE, W.C.

If we now glance briefly at the variations of each element and the effect on the character of the product, we observe—

1. Phosphorus increased from 0·47 to 0·61 per cent. This was probably due to loss of material during oxidation, the phosphorus remaining in the metal. A little may also have been gained in other ways; but I am not aware of evidence to show that an increase of phosphorus within the limits mentioned would materially affect the product.

2. Manganese decreased from 1·75 to 0·12 per cent. This would tend to improve the metal during the earlier meltings.

3. Silicon was reduced from 4·22 to 1·88 per cent. The first effect of this reduction was to produce softer metal and lower combined carbon, since silicon was present in quantity in excess of that necessary for the softest metal. On further reducing the silicon, the metal became stronger and harder. But in these experiments the reduction was not carried sufficiently far to cause any deterioration due to deficiency of silicon; for under ordinary circumstances a metal with 1·88 per cent. of silicon would be soft, close-grained, grey, and of very considerable tenacity.

4. Sulphur increased from 0·03 to 0·20 per cent., and in this change we have one of the most important alterations which took place. In the paper recently read before the Iron and Steel Institute, I have stated "that 1 part of sulphur neutralises the effect of at least from 5 to 10 parts of silicon," and have suggested that—

For soft foundry iron, sulphur should not exceed	0·13 p. c.
,, hard or mottled iron, about	0·20 ,,
,, white iron, over	0·25 ,,

Now in the sixteenth melting we find that silicon, which tends to produce grey iron, has been reduced to 1·88 per cent., while sulphur, which tends to produce white iron, has increased to 0·2 per cent., or just to that amount which is favourable for the production of hard or mottled iron. The bar itself is described as being white on the outside, with about three-sixteenths of an inch grey in the middle, and therefore agreeing with what might be anticipated from its composition.

5. The total carbon underwent very slight alteration. The slight apparent increase at first is quite in accordance with what has been observed in the puddling process and Bessemer converter.

6. The combined carbon was reduced during the earlier meltings, but again increased as the metal became harder, reaching a maximum of over 2 per cent. These changes are dependent on the alterations in the other elements present, especially sulphur and silicon.

In conclusion, I would express my belief that the experiments of Sir

W. Fairbairn, with the corrected analyses, afford us valuable information as to the influence of chemical composition on the mechanical value of cast iron. But they do not afford information as to the effect of remelting, except under the circumstances of these experiments. This effect will obviously depend on the original composition of the iron, and the character of the changes which take place in its constituents during remelting. At present I am not aware that we have any valid grounds for asserting that remelting, *apart from chemical change*, is either beneficial or otherwise on the character of the product.

LII.—*Some Ammonium Compounds and other Derivatives of α-1′ Hydroxyquinoline.*

By C. A. Kohn, B.Sc., Ph.D.

The following investigation was conducted under the guidance of Prof. Otto Fischer, of Erlangen, and is a continuation of his researches on α-1′ hydroxyquinoline (Bedall and O. Fischer, *Ber. Ber.*, **14**, 442, 1366; **16**, 712; O. Fischer and Renouf, *ibid.*, **17**, 755), especially in the direction of the ammonium bases connected therewith. I take this opportunity of expressing my sincerest thanks for his invaluable aid and kindly advice accorded to me while engaged in this work.

The nature of the compounds formed by the action of silver oxide and the caustic alkalis on the addition products which quinoline, pyridine, and acridine form with methyl iodide, has long been discussed, and in spite of the numerous investigations by Claus, Bernthsen, Hofmann, and others, still remains to some extent obscure. These compounds differ in many respects from the quarternary bases derived from the fatty, and from most members of the aromatic series, especially as regards their formation by the action of the hydrates of potassium and sodium on the corresponding ammonium iodides and in their solubilities in water, ether, benzene, &c.

Whilst the pyridine-ammonium bases possess these abnormal properties, the classical researches of Hofmann on piperidine and conine (*Ber. Ber.*, **14**, 659, 705) have proved that the reduced pyridines form true quarternary compounds. This holds good also for the reduced quinolines, as Feer and Königs (*Ber. Ber.*, **18**, 2388) have shown to be the case with hydromethylquinoline (kairolin). Hydroxyhydromethyl- and ethyl-quinoline also behave normally as regards their

ammonium compounds except in one point. By the action of solid caustic potash on the kairin ammonium iodides, an isomeric change takes place, the added alkyl-group and the hydrogen of the hydroxyl exchanging places, forming an ether of the original compound. Hydroxyhydromethylquinoline methiodide when thus treated yields methoxyhydromethylquinoline. Griess (*Ber. Ber.*, 13, 246, 647) noticed a similar reaction in the distillation of trimethylphenol-ammonium, the methyl ether of dimethylamidophenol being formed—

$$C_6H_4\Big\langle\begin{matrix}O\\ |\\ N(CH_3)_3\end{matrix} \quad + \quad C_6H_4\Big\langle\begin{matrix}OCH_3\\ \\ N(CH_3)_2\end{matrix}\ .$$

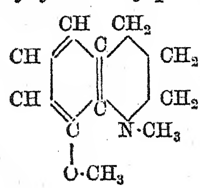
While, however, in Griess's experiments this transference of the methyl-group occurs in one and the same benzene-ring, the following results go to show that it can also take place when the hydroxyl is situated in an adjoining ring.

Hydroxyhydromethylquinoline Methiodide, $C_{10}H_{13}NO,CH_3I$.

Hydroxyhydromethylquinoline, which is obtained by precipitating the hydrochloride with sodium carbonate, is dissolved in methyl alcohol, and the solution heated for $1\frac{1}{2}$ hours on the water-bath with a small excess of methyl iodide. The wood-spirit and excess of methyl iodide are then distilled off, when the ammonium iodide remains as a crystalline mass. By one recrystallisation from wood-spirit, with the addition of a little animal charcoal, it is obtained pure in the form of long white prisms melting at 215—216°. It is easily soluble in water, sparingly in cold wood-spirit and alcohol, but readily on warming. On adding ether to an alcoholic or wood-spirit solution of this compound, it is precipitated in fine white prisms.

	Found.	Calculated for $C_{10}H_{13}NO \cdot CH_3I$.
I..........	41·51	41·64 per cent.

Methoxyhydromethylquinoline.

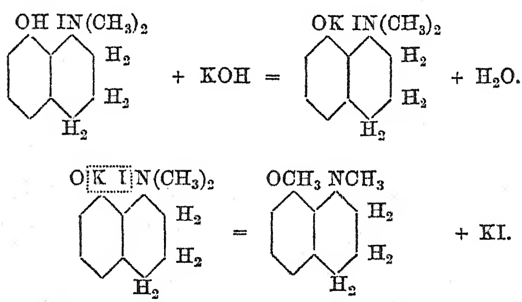


The above ammonium iodide distils almost unchanged, a small quantity of methyl iodide only being given off; but, as has been

already mentioned, by the action of caustic potash the iodine is removed and methoxyhydromethylquinoline is formed. The best yield (about 50 per cent. of the ammonium iodide used) is obtained by thoroughly mixing 10 grams of hydroxyhydromethylquinoline methiodide with 20 grams of finely powdered caustic potash and heating the whole in a small retort. After warming for a short time, the reaction sets in, and the mixture separates into two layers: the upper oily layer distils over completely on further heating. To purify the distillate, it is taken up with ether, and the ethereal solution washed and dried over caustic potash. On distilling off the ether, the new base is left as a pale yellow oil, which boils without decomposition at 256—258° (uncorr.).

	Found.	Calculated for $C_{11}H_{15}NO$.
C	74·16	74·58 per cent.
H	8·48	8·47 „

The formation of a methyl ether of hydroxyhydromethylquinoline by the action of caustic potash on hydroxyhydromethylquinoline methiodide, is to be explained as follows:—The potassium-derivative of hydroxyhydromethylquinoline methiodide is first formed, and this decomposes with elimination of potassium iodide, the methyl-group taking the place of the potassium thus removed, as shown in the following equations:—



Of the salts of this base, the following deserve mention:—The *platinochloride* is obtained in yellow prisms on adding platinum chloride to a solution of the base in hydrochloric acid. It is readily soluble in warm water, melts and decomposes at 199°, and contains no water of crystallisation.

	Found.	Calculated for $(C_{11}H_{15}NO)_2,H_2PtCl_6$.
Pt..........	25·58	25·47 per cent.

By the addition of concentrated sulphuric acid to an alcoholic solu-

tion of the base, an *acid sulphate* is obtained. It forms white prisms, which are easily soluble both in water and in alcohol.

	Found.	Calculated for $(C_{11}H_{15}NO),H_2SO_4$.
S	11·81	11·64 per cent.

The *hydrochloride* is very easily soluble. It is obtained in small prisms on allowing an alcoholic solution of the base, to which hydrochloric acid has been added, to remain for some time over lime and sulphuric acid in a vacuum.

Methoxyhydromethylquinoline is characterised by the following reactions:—With sodium nitrite in a slightly acid solution, a carmine-red coloration is obtained; on standing, a yellow precipitate forms. In a dilute sulphuric acid solution of the base, ferric chloride gives a rose-red coloration, potassium ferrocyanide a white flocculent precipitate.

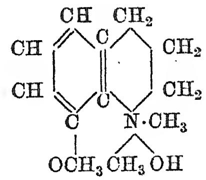
In order to prove that the product of the action of potash on the ammonium iodide of methylkairin is really a methyl ether of hydroxyhydromethylquinoline, it was prepared directly from the latter. It is best to start from its sodium salt, which can be obtained by dissolving the base in soda, and allowing it to stand; after a short time the sodium salt separates in a crystalline form. This is dried on a porous plate, and heated with wood-spirit and methyl iodide in a closed tube for several hours, at 130°. The methoxyhydromethylquinoline thus obtained was identical with that obtained from the ammonium iodide by the action of potash. It boiled at 256—258°, gave the characteristic reactions with sodium nitrite, ferric chloride, and potassium ferrocyanide, and also the platinochloride, which melted with decomposition at 199°. A little methoxyhydromethylquinoline methiodide was also formed in the reaction.

Methoxyhydromethylquinoline Methiodide, $C_{11}H_{15}NO,CH_3I$.

Methoxyhydromethylquinoline readily combines with methyl iodide under similar conditions to hydroxyhydromethylquinoline. The ammonium iodide thus obtained is easily soluble in water, alcohol, wood-spirit, and chloroform. It crystallises from wood-spirit in long white prisms, which melt at 175°, but soften at 173°. When heated with caustic potash, it distils unchanged (m. p. 175°).

	Found.	Calculated for $C_{11}H_{15}NO\cdot CH_3\cdot I$.
I	39·63	39·81 per cent.

Methoxyhydrodimethylquinolium Hydroxide.



By treating the above compound with moist silver oxide, the iodine is displaced by hydroxyl. The oxide of silver is added till the solution contains no more iodine; it is then evaporated down to a small bulk on the water-bath, at a gentle heat (60—70°); and lastly, further concentrated in the exsiccator. A crystalline mass remains, consisting of the hydroxide and its carbonate. The hydroxide is extremely hygroscopic, has an alkaline reaction, liberates ammonia from its salts, and combines very readily with the carbon dioxide of the air, so that if the above-mentioned crystalline mass be dissolved in water and the solution evaporated, well-defined crystals of the carbonate will be obtained. The base is very readily soluble in alcohol and wood-spirit, insoluble in ether, chloroform, and benzene.

With hydrochloric acid and platinum chloride, it forms a double salt, which crystallises in beautiful yellow prisms. This gave the following result on analysis :—

	Found.	Calculated for $(C_{11}H_{15}NO,CH_3Cl)_2,PtCl_4$.
C	36·39	36·39 per cent.
H	4·78	4·55 ,,
Pt	24·34	24·57 ,,

This salt contains no water of crystallisation, and melts at 200° with decomposition.

This hydroxide behaves quite normally on heating, being resolved into methyl alcohol and methoxyhydromethylquinoline. A concentrated freshly prepared aqueous solution was heated on an oil-bath, in a flask connected with a condenser. Between 100° and 130° an oil, easily recognised as methoxyhydromethylquinoline, distilled over with the water, the residue in the flask consisting wholly of this base. Its boiling point was 256—258°; also it gave the platinochloride (m. p. 199°), and the above mentioned reactions.

The following equation represents this decomposition :—

$$C_9H_9(OCH_3)N(CH_3)_2{\cdot}OH = C_9H_9(OCH_3)N{\cdot}CH_3 + CH_3{\cdot}OH.$$

The presence of the methyl alcohol could not be proved with certainty, owing to its small amount.

Hydroxyhydroethylquinoline Ethiodide, $C_{11}H_{15}NO,C_2H_5I$.

Hydroxyhydroethylquinoline, heated with ethyl iodide in alcoholic solution on the water-bath, gives this ammonium iodide, which when crystallised from water forms colourless prisms, melting at 160°. It is slightly more soluble in alcohol and wood-spirit than the corresponding methyl compound.

	Found.	Calculated for $C_{11}H_{15}NO,C_2H_5I$.
I	38·00	38·14 per cent.

Treated with caustic potash, this compound yields ethoxyhydroethylquinoline, previously obtained by O. Fischer (*Ber. Ber.*, **17**, 755), by the action of ethyl bromide on ethoxyhydroquinoline.

The reaction resembles exactly that with hydroxyhydromethylquinoline methiodide, the ethylkairin distilling over and collecting in the receiver, where it soon solidifies. Its boiling point was observed at 269—271° (uncorr.): it was further identified by the formation of its characteristic picrate, which crystallises in yellow prisms.

Ethoxyhydroethylquinoline Ethiodide, $C_{13}H_{19}NO,C_2H_5I$.

This is prepared similarly to the previous ammonium iodides. It is very easily soluble in water, alcohol, and wood-spirit. It can be obtained in long colourless prisms, melting at 136—137°, by adding ether to its alcoholic solution.

	Found.	Calculated for $C_{13}H_{19}NO,C_2H_5I$.
I	35·44	35·18 per cent.

Ethoxyhydrodiethylquinolium Hydroxide, $C_{13}H_{19}NO,C_2H_5{\cdot}OH$.

The above ammonium iodide is readily transformed by means of moist silver oxide into the corresponding hydroxide, which closely resembles the methyl compound in its properties. It is equally hygroscopic, and absorbs the carbon dioxide from the air with the same avidity. The platinochloride forms short orange-yellow prisms, which melt with decomposition at 183°. They contain no water of crystallisation:—

	Found.	Calculated for $(C_{13}H_{19}NO,C_2H_5Cl)_2PtCl_4$.
Pt..........	22·46	22·23 per cent.

On heating an aqueous solution of the hydroxide, water and a little ethylkairin distilled over between 100—130°. The residue consisted wholly of ethylkairin. It boiled at 269—271°, and gave the

characteristic picrate, crystallising in yellow prisms. The distillate was acidified and redistilled, but no trace of alcohol could be found in the distillate by means of the iodoform reaction. Hence it is probable that the alcohol was resolved into ethylene and water, as is known to be the case on heating tetrethylammonium hydroxide.

Hydroxyhydromethylquinoline Benzylchloride, $C_{10}H_{13}NO,C_7H_7Cl$.

In order to prove whether, in point of fact, the action of caustic potash on the methiodide and ethiodide of kairin gives rise to the transference of the added alkyl-group, I tried to obtain the benzyl chloride compound of hydroxyhydromethylquinoline. Unfortunately, however, I was unable to prepare it in a pure state. By heating hydroxyhydromethylquinoline with benzyl chloride in a closed tube at 170—180°, a red product is obtained, from which a very minute quantity of small colourless prisms was separated. The solid product contained in the tubes was mixed with solid caustic potash and heated, when a reaction set in similar to that with the methiodide and ethiodide of kairin, and a yellow oil boiling at about 300° distilled over. This oil possessed strongly basic properties, and gave a sparingly soluble amorphous salt with platinum chloride; this, however, owing to the small amount of the base available, could not be obtained in a pure state. Although these results are far from being satisfactory, they tend to show that the compound thus formed is a benzyl ether of hydroxyhydromethylquinoline, and therefore that it is the added group which has been transferred. A methyl ether of hydroxyhydrobenzylquinoline would not, in all probability, show strong basic properties. Further, by heating the sodium salt of hydroxyhydromethylquinoline with benzyl chloride, an oil, boiling at 300—325°, was obtained, which also gave a sparingly soluble amorphous platinochloride. The two products, therefore, appear to be identical.

Of the remaining kairin-derivatives to be described, acetylkairin and hydroxyhydroethylenequinoline possess a physiological as well as a chemical interest.

It is now generally admitted that a quinoline or pyridine group is directly connected with the constitution of many of the alkaloïds, and this view has been very materially supported by the investigation of the physiological properties of many synthetically prepared derivatives of quinoline and pyridine.

According to Donath (*Ber. Ber.*, **14**, 178—179), quinoline itself possesses antipyretic, antiseptic, and antizymotic properties, but acts injuriously on the system. The hydroxy-derivatives of quinoline, prepared by O. Fischer, have been very thoroughly investigated by

Filehne in regard to their physiological action. α-1′ Hydroxy- and methoxy-quinoline are poisonous, whilst the tetrahydrides of these compounds, namely, hydroxyhydroquinoline and methoxyhydroquinoline, exhibit a physiological action akin to that of quinine, but have unpleasant secondary actions, such as decomposing albumin, &c. The activity and instability of these substances were found, as a result of the above investigations, to be chiefly due to the presence of the unstable hydrogen-atom united with the nitrogen of the pyridine-ring, and in order to obtain a more stable molecule, Fischer prepared his so-called "kairin." The hydrochlorides of hydroxyhydromethylquinoline and -ethylquinoline are capable of reducing the temperature of the body in cases of fever to its normal state, and this without causing any unpleasant secondary action. Since its discovery (1881), kairin has been used with success as a febrifuge.

α-2′ Hydroxyethylquinoline, α-1′ ethoxyhydromethylquinoline, and also the hydromethylquinoline (kairolin) of Königs, all show a tendency to act like quinine, and differ only in the time the action lasts. It lasts the longest (15 to 16 hours) with the acid sulphate of α-1′ ethoxyhydroethylquinoline.

The acetyl-derivative of hydroxyhydroethylquinoline is so unstable that it was useless to investigate its physiological action. The action of the acid sulphate of hydroxyhydroethylenequinoline was investigated by Filehne. It is a febrifuge like kairin, but its action is far weaker, a fact in all probability due to its weaker basic properties. The investigations on this subject up to the present seem to show that the relative activity of these febrifuges bears a due proportion to their basicity.

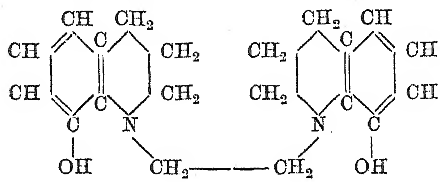
Acethydroxyhydroethylquinoline (Acetylkairin), $C_{11}H_{14}N(O{\cdot}C_2H_3O)$.

Hydroxyhydroethylquinoline is heated with sodium acetate and acetic anhydride for about three hours, and the whole then poured gradually into water, the mixture being cooled from time to time. After long standing, or on the addition of caustic soda solution, the acetylkairin separates out in the crystalline form. It is insoluble in water, and is readily purified by dissolving it in cold alcohol and precipitating by water. It dissolves very readily in ether, crystallising from this medium in thick prisms, which melt at 63—64°. In presence of acids or alkalis, it readily undergoes hydrolysis. An alcoholic solution of acetylkairin decomposes on exposure to the air.

	Found.	Calculated for ($C_{11}H_{14}NO{\cdot}C_2H_3O$).
C	70·82	71·23 per cent.
H	7·82	7·76 ,,

Benzoyl chloride also reacts very readily with kairin forming the benzoyl ether, a compound no longer possessing basic properties, easily soluble in ether and alcohol, and very readily decomposed into its constituents.

Hydroxyhydroethylenequinoline,



2 mols. of hydroxyhydroquinoline, prepared from hydroxyquinoline according to the data given by Bedall and O. Fischer (*Ber. Ber.*, **14**, 1366), are heated with 1 mol. of ethylene bromide in a closed tube at 150° for six hours. The hydrobromide of the new substance separates in the tube as a crystalline mass, and is best purified by recrystallisation from wood-spirit. It is thus obtained in small hard crystals, which are freed from any adhering colouring matter by washing them with alcohol. To obtain the base, the purified salt is dissolved in wood-spirit (it is very sparingly soluble both in water and in alcohol), and sodium carbonate is added, when it separates as a white crystalline precipitate. It may be readily separated from hydroxyhydroquinoline by recrystallisation from alcohol, when it is obtained in small silky prisms. Its melting point was found to be 233°.

Hydroxyhydroethylenequinoline is soluble in alcohol, wood-spirit, and light petroleum only on boiling, but dissolves in both chloroform and benzene in the cold. It is insoluble in water and in solutions of the caustic alkalis. The presence of the hydroxy-groups could only be proved by warming the base with alcohol till it was partially dissolved, and then adding a few drops of caustic soda. The whole dissolved immediately, the sodium salt separating after a few minutes in small crystals. These are easily soluble in water, but are decomposed almost directly, the unaltered base separating out:—

	Found.	Calculated for $C_{20}H_{24}N_2O_2$.
C	73·96	74·07 per cent.
H	7·43	7·41 ,,

By the linking of the two quinoline-rings, the basic as well as the acid properties of this compound are materially decreased. Hydroxyhydroethylenequinoline dissolves in dilute mineral acids only on heating; it does not form any salts with acetic, tartaric, or citric acid,

To obtain the *hydrochloride*, the base is dissolved in chloroform, an equal volume of alcohol added to the solution, and then strong hydrochloric acid. After a short time the salt separates in small colourless prisms, which dissolve easily in wood-spirit, but are only very slightly soluble in water and alcohol. If platinum chloride be added to the chloroform alcoholic solution of the hydrochloride, a *platinochloride* is formed. This has a faint reddish colour, and is sparingly soluble both in water and alcohol. An *acid sulphate* can be obtained similarly to the hydrochloride; it dissolves readily in water and crystallises well. This salt decomposes gradually on standing, with separation of the base; this decomposition, which is readily effected by heat, is prevented by the presence of dilute acids.

Hydroxyhydroethylenequinoline gives many characteristic reactions. A dilute acid solution gives a yellow precipitate with sodium nitrite, and a white flocculent precipitate with potassium ferrocyanide. By adding ferric chloride to an alcoholic solution of the base, a beautiful violet coloration is obtained; an excess gives a brown-red colour. Ferrous sulphate also colours the alcoholic solution violet, whilst nitric acid produces with the base a carmine-red colour, which turns yellow on standing.

Dinitroethoxyhydroethylquinoline, $C_{13}H_{17}NO(NO_2)_2$.

The nitration of ethylkairin is readily effected, two nitro-groups being introduced, as is also the case with hydroxyquinoline (Bedall, *Inaug. Dissert.*, Munich). Ethoxyhydroethylquinoline is dissolved in strong sulphuric acid, and this solution is added to the requisite quantity of nitre also dissolved in sulphuric acid. The reaction is not at all violent and the mixture only becomes slightly warm. The product of the reaction is then poured into water, and the dinitroethylkairin precipitated with caustic soda. It is obtained in beautiful yellow prisms by recrystallisation from alcohol, and melts at 76—77°. This nitro-compound is basic and dissolves readily in strong acids.

	Found.	Calculated for $C_{13}H_{17}NO(NO_2)_2$.
N..........	14·54	14·24 per cent.

Feer and Königs (*Ber. Ber.*, **17**, 2388) nitrated hydromethylquinoline under similar conditions to the above, and obtained a mono-nitro-compound, so that the presence of the ethoxy-group in ethylkairin is probably the cause of its great activity.

LIII.—β-*Sulphophthalic Acid.*

By A. Rée, Ph.D.

Although phthalic acid and several of its derivatives have been carefully examined, notably nitro-amido- and hydroxy-phthalic acids, our knowledge of the properties and preparation of the two possible sulphophthalic acids has hitherto been very limited. Apart from the interest which attaches to the last-mentioned acids in themselves, it seemed probable they would also be suitable for the preparation of the two hydroxyphthalic acids. Some 20 years ago, Loew (*Annalen*, **143**, 259) published a short notice on the action of sulphuric anhydride on phthalic acid in sealed tubes at 100—105°. He obtained a small amount of an acid, but its properties did not correspond with those one would expect in a sulpho-conjugated phthalic acid. According to Loew, on boiling an aqueous solution of the acid or of its salts, decomposition ensued and sulphuric acid was liberated.

Jacobsen (*Ber.*, **14**, 42) obtained an acid salt of β-sulphaminephthalic acid by oxidising ortho-xylenesulphonamide with potassic permanganate.

The same salt, the formula of which Jacobsen gave as—

$$C_6H_3\begin{cases} SO_2NH_2(4) \\ COOK\ \ (2) \\ COOH\ \ (1) \end{cases} + 2H_2O.$$

was prepared by Remsen and Comstock (*Amer. Chem. J.*, **5**, 106) by the oxidation of naphthalene-β-sulphonamide, whilst naphthalene-α-sulphonamide gave derivatives of α-sulphophthalic acid.

Müller and Laiblin (*Ber.*, **18**, 1126) were the first to observe that β-sulphophthalic acid is formed by the action of nitric acid on dinitro-α-naphtholsulphonic acid, the potassium salt of which is well known in commerce as naphthol-yellow S., the formula of which, according to Lauterbach ["*Recherches sur quelques dérivés de l'acide monosulfonique du dinitronaphtole.*" Geneva, 1882], is $C_{10}H_4(NO_2)_2(OK)\cdot SO_3K$. As they neither published nor intended to make further use of this interesting discovery, we took up the study of the above reaction with the view of preparing considerable quantities of pure β-sulphophthalic acid. Only one difficulty was encountered, namely, that the residue left after oxidation with nitric acid was always yellow. We cannot account for this, except by assuming that there are traces of dinitro-α-naphthol (Martius yellow) in the naphthol-yellow S. used. Naphthol-yellow S. is prepared by the action of nitric acid on

α-naphtholtrisulphonic acid at a temperature not exceeding 50°. (German patent No. 10785). Now the latter also contains traces of naphtholdisulphonic acid, and this with nitric acid forms dinitronaphthol, which, in its turn, is only attacked by boiling with concentrated nitric acid.

Preparation of β-Sulphophthalic Acid from Naphthol-yellow S.

Naphthol-yellow S. is heated in the water-bath with thrice its weight of nitric acid (sp. gr. 1·33—1·38). As soon as the temperature rises above 50°, a violent reaction sets in, which continues even without further application of heat, until almost all the colouring matter is oxidised. The solution is then heated until the evolution of gas ceases and evaporated to dryness. The yellow residue, consisting of monopotassic β-sulphophthalate and potassic nitrate, is dissolved in hot water, and to this so much of a solution of baric chloride is added as corresponds with a primary salt of sulphophthalic acid. After filtering off small quantities of baric sulphate, the solution is evaporated to crystallisation and the acid barium salt recrystallised from hot water (to which a little hydrochloric acid has been added) until the colour no longer diminishes in intensity. The baric salt is thus obtained almost white, and is converted into the free acid by exact precipitation with sulphuric acid. On evaporating the filtrate—finally over the water-bath—until syrupy, and then drying in an air-bath below 100°, the hydrate of β-sulphophthalic acid is obtained as a crystalline mass of a greyish colour.

If β-sulphophthalic acid is to be used merely for the preparation of β-hydroxyphthalic acid, it is unnecessary to purify it by means of its barium salt. As, however, the presence of potassic nitrate would be disadvantageous in a fusion with caustic soda, it is advisable first to remove the potassium from naphthol-yellow S. by heating it with a considerable amount of hydrochloric acid; on cooling, dinitronaphtholsulphonic acid separates in fine needles, and is then oxidised by heating with three parts of nitric acid (sp. gr. 1·33—1·38). On evaporating, free sulphophthalic acid is obtained, which can be easily converted into hydroxyphthalic acid, as described in the following communication (p. 522).

The yield of sulphophthalic acid is quantitative, but a slight loss is entailed by purifying it by conversion into the baric salt.

Preparation of β-Sulphophthalic Acid from Phthalic Anhydride.

On repeating Loew's experiments, it was found that the acid he obtained was indeed sulphophthalic acid, but contrary to his state-

ment, boiling water dissolved the barium salt without decomposition. Fusion with caustic soda showed that the chief product formed by the action of sulphuric anhydride on phthalic acid was β-sulphophthalic acid.

As already observed, the publication of Loew on this subject is very incomplete, and it seemed worth while, therefore, to carry out this investigation more carefully, especially as phthalic anhydride is easily obtainable. We were more particularly desirous of improving the yield of sulphophthalic acid (Loew obtained less than 10 per cent.).

We first experimented in sealed tubes, like Loew, and found that phthalic anhydride may be almost entirely converted into its sulphoconjugated derivatives, by prolonged heating at 170—180° with fuming sulphuric acid containing a high percentage of anhydride. Heating under pressure, however, is entirely unnecessary and the process becomes very simple if carried out as follows:—

100 grams of phthalic anhydride dissolved in 150 grams of sulphuric acid containing 20—25 per cent. of anhydride, are heated at 200°, later at 210°, while a constant current of sulphuric anhydride vapour is passed into the solution. After about $6\frac{1}{2}$ hours the reaction may be looked on as complete, for on diluting a small quantity of the mixture with water and extracting with ether, not a trace of phthalic acid can be detected. On cooling, the contents of the flask are poured into water and the sulphuric acid exactly precipitated with baric hydrate or carbonate. The filtrate is treated with 5—10 c.c. of concentrated hydrochloric acid, then with a hot solution of 100 grams of baric hydrate, and evaporated to the crystallising point. On cooling, monobaric β-sulphophthalate is deposited, and purified by recrystallising it once from a little boiling water, when beautiful white crystals are obtained, these being entirely free from α-sulphophthalic acid, an accessory product, which remains in the mother-liquor.

To separate free β-sulphophthalic acid, a hot aqueous solution of the baric salt is treated in the way above described under the preparation of the acid from naphthol-yellow S., and the hydrate of sulphophthalic acid is then obtained as an almost colourless crystalline mass, representing about 80 per cent. of the theoretical yield, in other words 100 grams of phthalic anhydride gave nearly 150 grams of β-sulphophthalic hydrate.

Before proceeding to a description of this compound, we should like to make a few observations on *α-sulphophthalic acid*, which, as above mentioned, is also produced in this process. The amount being small, however, escaped notice at first, as the experiments were conducted on a small scale. The presence of another acid besides β-sulphophthalic acid was first suggested, when the latter, without being

first purified by means of the baric salt, was fused with caustic soda. The melt assumed a bluish-grey tint, this not being the case when pure β-sulphophthalic acid was similarly treated. After separating the β-hydroxyphthalic acid, which was of course the chief product formed, we were once successful in obtaining traces of an acid melting at 155°, and giving an intense bluish-violet coloration with ferric chloride. Both these facts point to salicylic acid, but they do not furnish us with sufficient evidence for deciding the question whether we were really dealing with that acid. The quantity at our disposal was too small for further investigation. We, moreover, never again succeeded in obtaining an acid having the properties of salicylic acid. It is, however, possible that this acid is formed from α-hydroxyphthalic acid under favourable circumstances (*Ber.*, **18**, 1629), and α-sulphophthalic acid was undoubtedly detected in the following way:—

The barium was precipitated from the mother-liquors of basic β-sulphophthalate by a moderate excess of sulphuric acid, and the filtrate evaporated. After cooling and standing some time, nodules consisting of small microscopical needles separated—a property never observed in the case of β-sulphophthalic acid, but one characteristic of a number of sulphonic acids which are less soluble in very dilute acid than in pure water. Both Remsen and Comstock (*Amer. Chem. J.*, **5**, 106—111) and Stokes (*ibid.*, **6**, 260—262) who worked with α-sulphophthalic acid, seem to have overlooked this property.

The normal barium salt was analysed. 0·1962 gram dried at 250° gave 0·1514 gram $BaSO_4$.

	Calculated for $[C_6H_3(COO)_2 \cdot SO_3]_2Ba_3$.	Found.
Ba..........	45·82	45·37 per cent.

It was sparingly soluble in hot water, and crystallised in silky needles which had the appearance of small transparent plates under the microscope.

The best proof that the above acid is really α-sulphophthalic acid is, however, adduced from the fact that fusion with caustic soda converts it into Miller's α-hydroxyphthalic acid. To this end, a portion of the mother-liquors from baric β-sulphophthalate were freed from barium, neutralised with soda, evaporated, and the sodic salts fused with sodic hydrate at a temperature of 200—210°. The melt having been softened in water, excess of hydrochloric acid was added, the solution concentrated and extracted with ether. The residue remaining on evaporating the ether consisted of α- and β-hydroxyphthalic acids and metahydroxybenzoic acid. The first two could be partly removed by crystallising the product from a little water; being less

soluble than α-hydroxyphthalic acid, they came out first. The mother-liquor was then evaporated, the residue dissolved in as little ether as possible, and precipitated fractionally with benzene, when β-hydroxyphthalic acid was the first to separate, the solution finally containing only the α-hydroxy-acid. After distilling off the ether and benzene and crystallising from water with use of animal charcoal, short hard prisms were obtained giving all the reactions which Miller (*Annalen*, **208**, 247) and Jacobsen (*Ber.*, **16**, 1962) describe as characteristic of α-hydroxyphthalic acid. The melting point was 195°, the anhydride melting at 146°.

An analysis of the silver salt gave the following results:—0·2028 gram yielded 0·1099 gram AgCl.

	Calculated for $C_6H_3(OH)(COOAg)_2$.	Found.
Ag......	54·54 per cent.	54·19 per cent.

The acid was coloured an intense cherry-red by ferric chloride, and was readily soluble in cold water.

The hydrate of β-sulphophthalic acid, $C_6H_3(SO_3H)(COOH)_2 + H_2O$ consists of long spikes clustered in rosettes if obtained by prolonged heating in an air-bath at 95°.

Analyses of the substance dried to a constant weight at 95° gave the following data:—

I.	0·2048	gram gave	0·2723	gram CO_2 and	0·0535	gram H_2O.
II.	0·2672	,,	0·3564	,,	0·0800	,,
III.	0·2394	,,	0·3182	,,	0·0668	,,

	Calculated for $C_6H_3(SO_3H)(COOH)_2 + H_2O$.	Found. I.	Found. II.	Found. III.	
C....	36·36 per cent.	36·28	36·38	36·25	per cent.
H...	3·33 ,,	2·89	3·33	3·10	,,

The hydrate is very hygroscopic and moderately soluble in alcohol, insoluble in ether. On acidifying an aqueous solution with a mineral acid and concentrating, no crystallisation takes place.

The melting point is about 138—140°. The hydrate obtained by means of naphthol-yellow S., if slowly heated, melts a little above 100°, losing water at the same time; this is probably due to a slight impurity. By heating to 140°, 1 mol. H_2O, corresponding with that of the hydrate, is given off.

0·4385 gram lost 0·0301 gram H_2O. Calculated, 6·82 per cent.; found, 6·87 per cent.

The *β-sulphophthalic acid* formed is a thick syrup.

I. 0·2212 gram dried at 120°* gave 0·3134 gram CO_2 and 0·0509 gram H_2O.

II. 0·1766 gram dried at 140° gave 0·2500 gram CO_2 and 0·0432 gram H_2O.

	Calculated for $C_6H_3(SO_3H)(COOH)_2$.	Found. I.	Found. II.
C....	39·02 per cent.	38·65	38·62 per cent.
H ...	2·44 ,,	2·58	2·72 ,,

The *anhydride* is produced by prolonged heating at 180°.

0·4028 gram lost 0·0292 gram H_2O. Calculated, 7·32 per cent.; found, 7·25 per cent.

It is a hard, brown, hygroscopic mass.

Notwithstanding its brown colour, it was only slightly decomposed, for a solution in water contained no sulphuric acid and was readily decolorised by animal charcoal.

We preferred to employ sulphophthalic acid prepared from phthalic acid for the experiments for the preparation of hydroxyphthalic acid. It may be also added that we found the hydrate more convenient as a starting part than the acid or its anhydride, seeing that it is the least hygroscopic of the three, and is most easily obtained pure.

The *normal baric salt*, $[C_6H_3(SO_3)(COO)_2]_2Ba_3$, is formed by adding baric hydrate to a solution of the acid until neutral, or by boiling the latter with baric carbonate. According to Loew, an acid salt is formed in the latter case. It crystallises in fine silky needles or small brilliant plates, having the appearance of pointed prisms under the microscope. The salt contains a varying amount of water of crystallisation according to the temperature at which it is deposited. Part of the water of crystallisation is lost on attempting to obtain the salt air-dry; it is only entirely removed at 250°.

I. 0·2042 gram dried at 250° gave 0·7568 gram $BaSO_4$.

II.† 0·2021 gram gave 0·1568 gram $BaSO_4$.

	Calculated for $[C_6H_3(SO_3)(COO)_2]Ba_3$.	Found. I.	Found. II.
Ba....	45·82 per cent.	45·75	45·62 per cent.

Once separated, the normal salt is very sparingly soluble in either cold or hot water, insoluble in alcohol.

* The product used for Analysis I was obtained from naphthol-yellow S., and lost its water of crystallisation at 120°.

† A salt, prepared by boiling the acid solution with baric carbonate, was used for this analysis.

The *dibaric salt*, $C_6H_3(SO_3ba)(COOba)(COOH)$* + 2aq, may be obtained pure by dissolving the normal salt in water containing so much hydrochloric acid as is necessary for the formation of the dibaric compound, evaporating, and recrystallising from hot water. On cooling, long slender needle-shaped crystals are deposited.

0·4883 gram of the air-dried salt lost 0·0427 gram H_2O on heating at 150°.

0·2220 gram dried at 150° gave 0·1362 gram $BaSO_4$.

	Calculated for $C_6H_3(SO_3ba)(COOba)(COOH) + 2aq$.	Found.
aq	8·74 per cent.	8·70 per cent.

	Calculated for $C_6H_3(SO_3ba)(COOba)(COOH)$.	Found.
Ba	35·96 per cent.	36·06 per cent.

On dissolving either this salt or the neutral one in a slight excess of dilute hydrochloric acid and evaporating—

The *monobaric salt*, $C_6H_3(SO_3ba)(COOH)_2 + 2\frac{1}{2}H_2O$, crystallises on cooling in a characteristic way, the crystals having the appearance of short pointed prisms grouped in rosettes. The same salt is produced by evaporating solutions of baric chloride and of the acid; in the presence of a large excess of hydrochloric acid, however, baric chloride crystallises out, and not baric sulphophthalate.

The mono-salt is more readily soluble in water than the di-salt, especially in hot water. Thus 14·76 grams of boiling water when saturated with the salt contained 7·35 grams of the latter, and 33·6 grams of water at 15° were found to contain only 1·6 gram of the salt when saturated; whence 1 part of the air-dried salt requires for solution about 2 parts of boiling water and 21 parts of water at 15°.

The following numbers are the result of two analyses, I being that of a salt obtained by the oxidation of naphthol-yellow S.; II, that of one obtained by the action of sulphuric anhydride on phthalic anhydride.

I. 0·6711 gram of the air-dried salt lost on heating at 150° 0·0849 gram H_2O.

2. 0·4516 gram dried at 150° gave 0·1692 gram $BaSO_4$.

II. 0·4064 gram of the air-dried salt lost on heating to 150° 0·0510 gram H_2O.

2. 0·1640 gram dried at 150° gave 0·0618 gram $BaSO_4$.

* $ba = \frac{Ba}{2}$.

	Calculated for $C_6H_3(SO_3ba)(COOH)_2 + 2\frac{1}{2}H_2O$.	Found. I.	II.
aq......	12·55 per cent.	12·65	12·55 per cent.

	Calculated for $C_6H_3(SO_3ba)(COOH)_2$.	Found. I.	II.
Ba......	21·85 per cent.	22·02	22·15 per cent.

As will be seen from the formula of this salt, it should be possible to convert it into a compound which is both salt and anhydride, and this is indeed easily accomplished by heating it at 250°.

0·4549 gram dried at 150° lost, on heating at 250°, 0·0260 gram H_2O.
0·1588 gram dried at 250° gave 0·0626 gram $BaSO_4$. Calculated for loss of 1 mol. of water, 5·71 per cent.; found, 5·74 per cent.

	Calculated for $C_6H_3(SO_3ba)<^{CO}_{CO}>O$.	Found.
Ba	23·18 per cent.	23·18 per cent.

The baric anhydro-salt is a white powder, and is easily converted by boiling water into the original mono-salt.

The normal potassic salt is very soluble in water. It may be obtained by adding alcohol to a solution of sulphophthalic acid which has been neutralised with potassic carbonate. The oil which is first deposited solidifies after some time. *The monopotassic salt*,

$$C_6H_3(SO_3K)(COOH) + 2H_2O,$$

separates in long, brilliant needles on evaporating solutions of sulphophthalic acid and potassic chloride. It was recrystallised and analysed.

1·0410 gram of air-dried salt lost 0·1183 gram H_2O on heating at 150°.
0·1736 gram dried at 150° gave 0·0530 gram K_2SO_4.

	Calculated for $C_6H_3(SO_3K)(COOH)_2 + 2H_2O$.	Found.
aq	11·25 per cent.	11·36 per cent.

	Calculated for $C_6H_3(SO_3K)(COOH)_2$.	Found.
K	13·73 per cent.	13·69 per cent.

It is readily soluble in water, insoluble in alcohol.

The normal sodic salt is very soluble, and crystallises in microscopical needles. *The normal calcic salt*, formed by adding calcic chloride to a solution of sulphophthalic acid previously neutralised

with ammonia, is an amorphous powder readily soluble in water. *The normal plumbic salt* is obtained as an amorphous powder on mixing aqueous solutions of plumbic acetate and sulphophthalic acid. It is almost insoluble in water. Hot water containing acetic acid dissolves it, and on cooling the same salt separates.

The di-ammonic salt, $C_6H_3(SO_3NH_4)(COO{\cdot}NH_4){\cdot}COOH + 1\frac{1}{2}H_2O$. On evaporating aqueous solutions of β-sulphophthalic acid which have been neutralised or made alkaline with ammonia, the solution is found to have an acid reaction after a short time. To prepare the pure salt, it is advisable to neutralise two-thirds of a solution of sulphophthalic acid with ammonia, then to add the other third and evaporate over the water-bath. After drying a short time at 100°, the mass is pulverised and boiled with 20 times its weight of alcohol, to which water is gradually added until the powder has just dissolved. On cooling, the solution deposits very fine needles, which are recrystallised in a similar way for analysis.

0·2920 gram of air-dried salt gave 0·0258 gram.

	Calculated for $C_6H_3(SO_3NH_4)(COO{\cdot}NH_4){\cdot}COOH + 1\frac{1}{2}H_2O$.	Found.
aq	8·80 per cent.	8·84 per cent.

That this is really a di-salt was proved by the following analyses of the substance dried at 100°:—

I. 0·2010 gram gave 0·2526 gram CO_2 and 0·0812 gram H_2O.
II. 0·2442 gram gave 22 c.c. N at 13°, and 719 mm. bar. pressure.

	Calculated for $C_6H_3(SO_3NH_4)(COO{\cdot}NH_4){\cdot}COOH$.	Found. I.	II.	
C....	34·29 per cent.	34·27	—	per cent.
H...	4·29 ,,	4·48	—	,,
N...	10·00 ,,	—	10·08	,,

It seemed likely that by heating above 100° an imide of β-sulphophthalic acid would be formed. Below 150° there was no loss in weight, but on further heating, especially between 165—190°, a decrease corresponding with 2 mols. H_2O was observed. We were unable by gradually raising the temperature to effect the loss of only 1 mol. H_2O.

2·6128 grams dried at 100° lost, on heating at 190°, 0·3402 gram H_2O. Calculated for the loss of $2H_2O$ 12·85 per cent., found 13·02 per cent.

The question now arose whether the substance thus formed is really the ammonic salt of an imide—

$$C_6H_3(SO_3NH_4)<\begin{smallmatrix}CO\\CO\end{smallmatrix}>NH, \text{ or } C_6H_3(SO_3NH_4)<\begin{smallmatrix}-CO-\\C(NH)\end{smallmatrix}>O.$$

or whether it must be regarded as a diamide of the formula—

$$C_6H_3(SO_2NH_2)(CONH_2)\cdot COOH.$$

As its reaction is neutral, however, this precludes the possibility of the latter alternative, and the compound may therefore be looked on as *ammonic sulphophthalimide*. It is purified by crystallising it from alcohol in the same way as described for ammonic sulphophthalate, animal charcoal being employed to decolorise it. By evaporating in a vacuum over sulphuric acid, brilliant monosymmetrical prisms were obtained.

Analyses of the salt dried at 100° gave the following results:—

I. 0·2832 gram gave 30·6 c.c. N at 16°, and 720 mm. bar. pressure.

II. 0·1994 gram gave 20·5 c.c. N at 10°, and 712 mm. bar. pressure.

	Calculated for $C_6H_3(SO_3NH_4)(CO)_2NH$.	Found. I.	Found. II.	
N......	11·47	11·89	11·53	per cent.

Its aqueous solution is gradually decomposed by boiling, and the salt is sparingly soluble in boiling alcohol (95 per cent.). Heated in a bent tube closed at one end, it melts at about 300°, sulphur dioxide being evolved and the greater part carbonised; at the same time, small glittering plates collect in the colder part of the tube, consisting, as their melting point (220°) and other properties showed, of phthalimide.

In order to obtain sulphophthalimide itself, it seemed practicable to prepare the lead salt. By evaporating aqueous solutions of ammonic sulphophthalimide and acetate of lead over the water-bath sulphophthalate of lead was deposited, as an analysis showed (calculated 56·10 per cent. Pb; found, 55·65 per cent.). To prevent decomposition, very dilute aqueous solutions (1 : 5) of the above products were mixed and allowed to evaporate slowly over sulphuric acid in a vacuum. Very brilliant fine prisms were obtained in this way, sparingly soluble in cold water, moderately in warm water. Unfortunately, however, this product—of most inviting appearance—proved not to be a salt of sulphophthalimide. It lost 10·13 per cent. of water at 100°, and the salt dried at 100° was found to contain 42·21 per cent. and 42·04 per cent. of lead.

Professor Soret was so kind as to measure the crystals of ammonic β-sulphophthalimide. He sent us the following account:—"Small

white crystals, apparently well formed. The angles, however, differ considerably in different specimens. The average of several determinations is adjoined.

Monosymmetrical prisms.

$$ZX = 92° \ 56'.$$

$$a : b : c = 0{\cdot}70766 : 1 : 0{\cdot}51903.$$

"Faces observed: (110) predominating and fairly developed; (100) uneven; (001) smaller, but constant; (111) varying; (001) very small and rare. The crystals are elongated in the direction of the Z axis—

Angles of the Normal.

(110) : (1$\bar{1}$0)	found	70° 30'*	calculated	—
(011) : (0$\bar{1}$1)	,,	54 49 *	,,	—
(110) : (011)	,,	72 23 *	,,	—
(100) : (011)	,,	86 58	,,	87° 24'
(100) : (111)	,,	54 58	,,	55 5
(111) : (1$\bar{1}$1)	,,	43 59	,,	44 24
(110) : (111)	,,	46 56	,,	46 39

"The optical axes are in the principal section; through (100) only a part of the hyperbole can be seen, and this points to an axis which is considerably inclined to Z (negative)"

Two chlorides of β-sulphophthalic acid were prepared, a trichloride and a monochloride.

The Trichloride, $C_6H_3(SO_2Cl)(COCl)_2$.

This is best obtained by heating β-sulphophthalic hydrate (1 mol.) with phosphorus pentachloride (4 mols.) in a closed tube at 150°. After distilling off the oxychloride, the trichloride remains as a thick oil.

0·2467 gram gave 0·3968 gram AgCl.

	Calculated for $C_6H_3(SO_2Cl)(COCl)_2$.	Found.
Cl......	39·52 per cent.	39·78 per cent.

When treated with cold water, the chloride is gradually converted into the solid monochloride.

On distilling it, decomposition ensues with considerable carbonisation, sulphur dioxide is evolved, and a deep yellow oil distils over; this, however, is not the trichloride of sulphophthalic acid, as after heating it with a solution of caustic soda it is possible to extract by

means of ether a substance which, after redistillation and recrystallisation from ether, is obtained in brilliant white crystals melting at 96°. On dissolving this in water, evaporating and drying, the melting point rose to 148°. As these two melting points represent those of a chlorophthalic anhydride and its corresponding acid, we were justified in assuming that a chloride of the latter acid had been formed by distilling sulphophthalic trichloride, as represented by the equation—

$$C_6H_3(SO_2Cl)(COCl)_2 = C_6H_3Cl(COCl)_2 + SO_3.$$

For the results of further investigations bearing on this subject we beg to refer to our next communication.

The Monochloride, $C_6H_3(SO_2Cl)(COOH)_2$.

This is easily prepared by heating sulphophthalic hydrate (1 mol.) with phosphorus pentachloride (3 mols.). After distilling off the oxychloride, the residue is mixed with ether, well shaken with water, and the ethereal solution, after drying over calcic chloride, is allowed to evaporate. A snowy white powder is then deposited, which, under the microscope, has the appearance of aggregates of needles grouped concentrically.

An analysis led to the following results:—

I. 0·2642 gram gave 0·1384 gram AgCl.

II. 0·1993 gram gave 0·2646 gram CO_2 and 0·0387 gram H_2O.

	Calculated for $C_6H_3(SO_2Cl)(COOH)_2$.	Found. I.	Found. II.	
C.....	36·29 per cent.	36·21	—	per cent.
H.....	1·89 ,,	2·12	—	,,
Cl.....	13·42 ,,	—	13·05	,,

The chloride is easily soluble in ether and alcohol, insoluble in chloroform, benzene, bisulphide of carbon, and light petroleum. When left in contact with water for a considerable time, no perceptible action was observed.

β-Sulphophthalic Amide, $C_6H_3(SO_2NH_2)(COOH)_2$.

To obtain it, the monochloride is carefully treated with an excess of ammonia and the solution evaporated to dryness on the water-bath. After decomposing the ammonic salt by again evaporating with a slight excess of hydrochloric acid, the powdered residue, consisting of ammonium chloride and the amide, is extracted with ether, and on evaporating the latter the pure amide remains.

0·2011 gram gave 0·2876 gram CO_2 and 0·0540 gram H_2O.

	Calculated for $C_6H_3(SO_2NH_2)(COOH)_2$.	Found.
C......	39·18 per cent.	39·00 per cent.
H......	2·86 ,,	2·98 ,,

The amide is soluble in water, alcohol, ether, and acetic acid, insoluble in chloroform, benzene, and light petroleum. On evaporating the aqueous solution, small transparent plates were obtained. As this substance decomposes on melting, it was not possible to determine the exact melting point; it lies between 192° and 202°.

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LIV.—*Some Compounds obtained by the Aid of β-Sulphophthalic Acid.*

By C. GRAEBE, Ph.D., and A. RÉE, Ph.D.

I. *β-Hydroxyphthalic Acid.*

By the action of nitric acid on phthalic acid, Miller (*Annalen*, **208**, 224) first obtained two nitrophthalic acids, one of which Baeyer (*Ber.*, **10**, 1079) converted into β-hydroxyphthalic acid by means of the diazo-compound, and from the other Miller (*Annalen*, **208**, 247) shortly afterwards prepared α-hydroxyphthalic acid. There is considerable difficulty in separating the two nitrophthalic acids, and in converting them into hydroxyphthalic acids.

It has been already mentioned in the previous paper that in preparing β-sulphophthalic acid for the purpose of converting it into β-hydroxyphthalic acid, it is advisable to oxidise dinitronaphtholsulphonic acid, and not its potassium salt (naphthol-yellow S.). After all the nitric acid has been expelled, the yellow residue is neutralised with sodium carbonate, and the sodium salt fused with two and a-half times its weight of caustic soda. The yield of hydroxyphthalic acid obtained was almost quantitative when the following precautions were employed. A quantity representing not more than 15 grams of sulphophthalic acid was fused for $2\frac{1}{2}$ hours, the mass being continually stirred, and maintained of such a consistence that it was just possible to stir it without difficulty, this being attained by the addition of water from time to time. The crucible was heated in an oil-bath, the temperature being maintained at 175°, and never

allowed to rise above 180°. The thermometer was placed in the fused mass and not in the oil-bath. After softening in water and acidifying strongly with hydrochloric acid, the β-hydroxyphthalic acid was extracted with ether, the ethereal solution treated with a little animal charcoal, and the ether evaporated; 8·3—8·5 grams of β-hydroxyphthalic acid in an almost pure state was thus obtained. It was purified by recrystallisation from a little warm water, and the traces of metahydroxybenzoic acid separated by heating it in a current of carbon dioxide at a temperature of 200—210°, when pure β-hydroxyphthalic anhydride sublimed. The results of two analyses of the acid are subjoined, both having been made with a product, not purified by means of the anhydride, and only crystallised from a little water. The acid used for analysis I still contained a little hydroxybenzoic acid, being taken from that portion which crystallised out first.

I. 0·2164 gram dried at 100° gave 0·4236 gram CO_2 and 0·0682 gram H_2O.

II. 0·2034 gram gave 0·3943 gram and 0·0610 gram H_2O.

	Calculated for $C_6H_3OH(COOH)_2$.	Found. I.	Found. II.
C......	52·74 per cent.	53·38	52·87 per cent.
H.....	3·30 ,,	3·50	3 30 ,,

(Hydroxybenzoic acid requires 60·87 per cent. C and 4·35 per cent. H.)

The pure acid was found to possess the characteristic properties described by Baeyer, the melting point being 185°, that of the anhydride 165°. Baeyer states (*Ber.*, **10**, 1079) that β-hydroxyphthalic acid is not changed by heating with dilute sulphuric acid at 180°. Now in the fusion with sodic hydrate, especially at temperatures above 200°, we found that the acid is partly converted into metahydroxybenzoic acid; also from analogy with β-amidophthalic acid, it seemed unlikely that β-hydroxyphthalic acid should be so stable when heated with dilute acids at 180°: our experiments confirm this view. 1 gram of the hydroxyphthalic acid was heated at 180° for six hours with 20 grams of hydrochloric acid (1 conct. acid : 1 water). The tube was opened, and the crystalline mass which had separated from the acid solution was found to consist of pure metahydroxybenzoic acid, melting at 200°, having a sweet taste, and giving no coloration with ferric chloride. To remove all doubt as to the acid being metahydroxybenzoic acid, the ethylic salt was prepared, and as expected, this crystallised from water in plates, melting at 72°.

This decomposition of β-hydroxyphthalic acid with formation of

metahydroxybenzoic acid is in accordance with observations made with several other substitution products of phthalic acid. There always seems to be a tendency for the production of stable metahydrobenzoic acid, and not of salicylic or parahydroxybenzoic acid.

β-Hydroxyphthalic acid may be obtained from phthalic acid through the sulpho-derivatives (see preceding communication, p. 513). After removing excess of sulphuric acid with baryta or lime, the α- and β-sulphophthalic acids are converted into their sodium salts and fused with sodic hydrate as above described.

The proportion of α-sulphophthalic acid in the mixture of the sulphonic acids is but small. The α-acid is chiefly converted into α-hydroxyphthalic acid at or above 200°, moreover this acid is more soluble in water than the corresponding β-hydroxy-acid. No difficulty is therefore experienced in obtaining the latter pure and free from α-hydroxyphthalic acid, the reaction with ferric chloride serving as a test of its purity; whereas concentrated solutions of β-hydroxyphthalic acid give only a faint yellowish-red tint with that reagent, traces of the α-acid are readily detected by the deep reddish-violet coloration produced.

Methylic β-Hydroxyphthalate, $C_6H_3(OH)(COOCH_3)_2$.

This is prepared in the usual way by saturating an alcoholic solution of the acid with hydrogen chloride, or by the action of methyl iodide on the silver salt. It crystallises from a hot aqueous solution in plates melting at 102°, and is soluble in the solvents usually employed.

I. 0·1751 gram dried at 100° gave 0·3638 gram CO_2 and 0·0721 gram H_2O.

II. 0·1674 gram gave 0·3497 gram CO_2 and 0·694 gram H_2O.

	Calculated for $C_6H_3(COOCH_3)_2{\cdot}OH$.	Found. I.	Found. II.
C......	57·14 per cent.	56·66	56·98 per cent.
H	4·76 ,,	4·57	4·61 ,,

β-Hydroxyphthalimide, $C_6H_3(OH){<}{\genfrac{}{}{0pt}{}{CO}{CO}}{>}NH$ or

$$C_6H_3(OH){<}{\genfrac{}{}{0pt}{}{\text{——}CO\text{——}}{CO(:NH)}}{>}O.$$

Dry ammonia gas was passed into fused β-hydroxyphthalic anhydride, which also contained traces of metahydroxybenzoic acid, until no more gas was absorbed. The cooler part of the vessel was

soon filled with brilliant needles, and towards the end of the operation a deep yellow oil distilled. It is advisable to stop the current of ammonia as soon as this yellow oil is observed. The crystalline mass is dissolved in boiling water, and the solution filtered to remove carbon and a substance which dissolves in alkali with a deep yellowish-red colour, but which was not examined further. The solution, on cooling, deposited small yellowish-white plates or needles, melting at 288—290°. These were sublimed, but the sublimate was still coloured, and did not become white even after repeatedly recrystallising it from water.

β-Hydroxyphthalimide is sparingly soluble in cold alcohol or ether, insoluble in chloroform, benzene, light petroleum, or carbon bisulphide. Hot acetic acid dissolves it readily. It closely resembles phthalimide.

One of us published a method some time ago (*Ber.*, **17**, 2599) for preparing phthalide from phthalimide, and we were interested in knowing whether this method might be used as successfully for the production of β-hydroxyphthalide from β-hydroxyphthalimide: 5 grams of the latter compound and 10 grams of water were heated over the water-bath with 10 grams of finely divided tin and 50 c.c. of concentrated hydrochloric acid, the latter being gradually added until all the tin had dissolved. Strips of zinc foil were then immersed in the solution, and finally boiled with it to precipitate all the tin, hydrochloric acid being added, if necessary, to keep all the hydroxyphthalidine in solution. The nitroso-derivative of the latter was then prepared by the gradual addition of sodium nitrite, when it separates as a finely crystalline yellow powder, melting at 170°. It gives Liebermann's reaction perfectly, and is only sparingly soluble in water, but readily in alcohol; almost insoluble in ether.

β-Hydroxyphthalide

is prepared from nitroso-β-hydroxyphthalidine by decomposing it with caustic soda while still moist, and the yellowish-red solution is heated gently until nitrogen ceases to be evolved; excess of hydrochloric acid is then added, when the greater part of the β-hydroxyphthalide separates. This is recrystallised from hot alcohol, the solution having been previously boiled with animal charcoal. The crystalline mass thus obtained consists of pointed prisms clustered in rosettes. The product is yellow, and the impurity is not removed by recrystallisation from alcohol or from boiling water.

0·2159 gram gave 0·5052 gram CO_2 and 0·0783 gram H_2O.

	Calculated for $C_6H_3(OH)<{CO-\atop CH_2}>O$.	Found.
C	64·00 per cent.	63·81 per cent.
H	4·00 „	4·03 „

β-Hydroxyphthalide sublimes in brilliant needles, and separates in the same form from boiling aqueous solutions. Neither ferric chloride nor alcoholic solutions of caustic potash produce any coloration. It melts at about 222°, but begins to soften at 210°.

β-Hydroxyphthalide is sparingly soluble in ether or chloroform, cold alcohol, and acetic acid. It is almost insoluble in bisulphide of carbon and benzene, entirely so in light petroleum.

We also tried the action of nitric acid on β-hydroxyphthalic acid, and publish for the present that when heated gently with thrice its weight of nitric acid (sp. gr. 1·33) a nitro-product is obtained which is readily soluble in ether and water, and crystallises from either of these solvents in almost rectangular flat rhombohedrons. It is easily converted into an amido-derivative.

II. *β-Chlorophthalic Acid.*

Until quite recently, very little was known of the two monochlorophthalic acids. One of them was obtained by Auerbach (*Jahresberichte über die Fortschritte d. Chemie*, 1880, 862) by passing a current of chlorine into a cold solution of phthalic acid in excess of alkali. The same acid has lately been prepared by Solari (private communication) by oxidising with nitric acid that dichloronaphthalene which is formed by heating naphthalene tetrachloride. Guareschi (*Ber.*, **19**, 134) obtained the same acid from a different dichloronaphthalene (m. p. 107°).

The other chlorophthalic acid was first mentioned by Alén (*Bull. Soc. Chim.*, **36**, 434), who prepared it by oxidising ε-dichloronaphthalene, Claus and Dehne (*Ber.*, **15**, 321) arriving at the same result independently of Alén.

The true constitution of these chlorophthalic acids was first proved by Krüger (*Ber.*, **18**, 1759), who obtained them from chlororthotoluic acids of known constitution. (Krüger, however, gives the melting point of β-chlorophthalic acid at 130—134°, whereas it is really 148°.) Unaware of this latter publication, Claus and Müller (*Ber.*, **18**, 3073) claimed to have proved the constitution of the two chlorophthalic acids. One of us, equally unaware of Krüger's research, then sent in a short notice to the *Berichte* (**18**, 3359), in which it was shown that the proof brought forward by Claus and Müller is insufficient, whereas the fact that it is possible to obtain a chlorophthalic acid of

the melting point 148° (the anhydride melting at 96°) from β-sulphophthalic acid by the aid of phosphorus pentachloride, must be looked on as conclusive evidence in favour of regarding the last-mentioned chlorophthalic acid as a β-derivative.

In describing the trichloride of β-sulphophthalic acid (see preceding paper), it was mentioned that this was converted by distillation into β-chlorophthalic chloride. As a considerable amount is carbonised in the process, we turned our attention to another method, first used by Kämmerer and Carius in their research on methylsulphobenzoic acid; this consists in the displacement of the sulphonic group by chlorine, by the action of phosphorus pentachloride at high temperatures.

On heating the hydrate of β-sulphophthalic acid (1 mol.) with phosphorus pentachloride (5 mols.) at 220°, it is entirely converted into chlorophthalic chloride, phosphorus oxychloride and thionyl chloride being the only bye-products, unless an excess of pentachloride is employed, when chloride of sulphur is also produced.

Chlorophthalic chloride boils at 275—276° (uncorr.) and fumes in the air. It is saponified with difficulty. To prepare larger quantities of chlorophthalic acid, the hydrate of β-sulphophthalic acid* was first converted into the monochloride by heating it with phosphorus pentachloride (3 mols.), and the liquid product was then heated with 2 mols. more of the pentachloride at 220°. There was no pressure in the tubes, phosphorus oxychloride and thionyl chloride were distilled off, and the residue treated with strong caustic potash. After acidifying with hydrochloric acid, the solution was extracted with ether; the chlorophthalic acid remaining after evaporation is pure enough for most purposes, the yield being moreover quantitative. To purify it further, it was distilled, and the anhydride dissolved in hot water. We found the melting point to be 148°, that given by Claus and Müller. The acid is very soluble in water, less so in water acidified with mineral acids. It is sparingly soluble in benzene, somewhat more soluble in chloroform or carbon bisulphide, insoluble in light petroleum.

* It will be generally found more practicable to use the potassium salt of sulphophthalic acid for this purpose instead of the hydrate, of which we happened to have large quantities. To this end, it is most convenient to oxidise naphthol-yellow S. with nitric acid (see preceding paper), and then to purify the monopotassic salt of β-sulphophthalic acid by repeated crystallisation from hot water containing a little hydrochloric acid. The potassium salt when heated at 250°, is converted into a compound of the formula $C_6H_3(SO_3K){<}{\genfrac{}{}{0pt}{}{CO}{CO}}{>}O$, which is then heated at 220° in closed tubes with 3 mols. of phosphorus pentachloride. In this way, chlorophthalic chloride, phosphorus oxychloride, thionyl chloride, and potassium chloride are formed.

The *anhydride* is obtained by distilling chlorophthalic acid. It solidifies in the receiver to a crystalline mass consisting of brilliant needles. On recrystallising it from ether, very fine brilliant plates, melting at 96—97°, are obtained. The anhydride boils 12·5° higher than phthalic anhydride, that is at 294·5° (thermometer enveloped in vapour, and pressure = 720 mm.).

An analysis gave the following numbers:—

0·2452 gram gave 0·1933 gram AgCl.

	Calculated for $C_6H_3Cl<^{CO}_{CO}>O$.	Found.
Cl........	19·45 per cent.	19·45 per cent.

It is readily soluble in alcohol, ether, benzene, chloroform, and acetic acid, fairly soluble in carbon bisulphide. In light petroleum, it dissolves only on boiling. We are indebted to Professor Soret for a measurement of the crystals obtained by crystallisation from ether. He sent us the following account:—

"The crystals are small and very brittle; the various determinations do not quite agree with one another, owing either to the extreme narrowness of some of the faces, or to the fact that the opposite faces are not exactly parallel to each other, this being the case with most of the crystals. They crystallise in prisms belonging to the anorthic system.

$$ZX = 109° \ 11' : XY = 115° \ 6' : YZ = 108° \ 40'.$$

$$a : b : c = 0·86625 : 1 : 1·15725.$$

"The crystals are elongated in the direction of X, and flattened in the direction of Y.

"Faces observed: (001) very much developed; (100) fairly developed and constant; (010)($1\bar{1}0$) rather small and varying; ($01\bar{1}$) (011) more constant; ($01\bar{3}$) small and varying; ($21\bar{1}$)($21\bar{3}$) very small.

Angles of the Normal.

(001) : (100)	calculated	—	found	57° 13′*
(100) : (010)	,,	—	,,	53 43 *
(001) : (010)	,,	—	,,	57 30 *
($1\bar{1}0$) : (100)	,,	—	,,	54 55 *
($00\bar{1}$) : ($00\bar{1}$)	,,	—	,,	70 57
(001) : (001)	,,	31° 41′	,,	31 37
(010) : ($01\bar{3}$)	,,	99 4	,,	99 39

"Through (001) an optical axis may be observed."

Methylic β-Chlorophthalate, $C_6H_3Cl(COOCH_3)_2$.

This was prepared in three ways—(1.) By passing dry hydrogen chloride into a methyl alcoholic solution of chlorophthalic anhydride. (2.) By the action of methyl iodide on the silver salt. (3.) By the action of methyl alcohol on the chloride. In each case, on crystallising from light petroleum, fine needles melting at 37° were obtained, soluble in the solvents usually employed.

The object in preparing this ethereal salt by three different methods was, if possible, to find an analogy between chlorophthalic acid and tetrachlorophthalic acid, the latter yielding different ethereal salts according to the methods used in its preparation (*Ber.*, **16**, 860).

This indeed, as one of us has already pointed out, might be expected if phthalyl chloride is thus constituted: $C_6H_4<{CO \atop CCl_2}>O$.

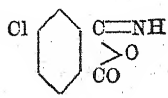
Why different substances were not obtained when different methods were used we are at a loss to understand. Perhaps we may venture to account for this unexpected result by assuming that unsymmetrical ethereal salts obtained by the aid of the chloride are unstable, and that under certain conditions they are converted into ethereal salts having a symmetrical constitution.

Ethylic β-chlorophthalate was obtained from the anhydride, and crystallises when exposed to low temperatures (−20°). The boiling point lies between 300—305°.

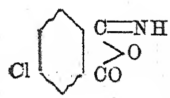
β-Chlorophthalimide, $C_6H_3Cl<{CO \atop C-}>NH$ or $C_6H_3Cl<{-CO- \atop C(:NH)}>O$.

A current of dry ammonia is passed into fused chlorophthalic anhydride until the gas is no longer absorbed. The crystalline mass obtained is dissolved in boiling water, from which, on cooling, small brilliant needles or plates separate, melting at 210—211°.

β-Chlorophthalimide is very similar to phthalimide. It sublimes readily, and is precipitated by acids from its solution in caustic potash. It is, however, less soluble in boiling water than phthalimide, being, moreover, but sparingly soluble in ether or cold alcohol, fairly soluble in warm benzene, chloroform, and acetic acid, insoluble in carbon bisulphide and light petroleum. Supposing phthalimide to be represented by the formula $C_6H_4<{-CO- \atop C(:NH)}>O$, it does not appear unlikely that two β-chlorophthalimides might be produced by the action of ammonia on β-chlorophthalic anhydride, respectively represented by the formulæ—



and



The product obtained, however, seemed to be perfectly homogeneous, for the melting point, 210—211°, did not alter on repeated recrystallisation.

$$\beta\text{-}Chlorofluoresceïn,\ CO{<}{}^{C_6H_3Cl}_{-O-}{>}C{<}{}^{C_6H_3(OH)}_{C_6H_3(OH)}{>}O.$$

1 gram of chlorophthalic anhydride was heated with 1·2 gram of resorcin at 200° until the mass became hard. This was then boiled with water, and the residue dissolved in caustic soda and precipitated with hydrochloric acid. β-Chlorofluoresceïn closely resembles fluoresceïn. It is almost insoluble in water, but dissolves in alcohol or ether when freshly precipitated. It changes to the crystalline form when dried and kept, at the same time becoming insoluble in alcohol or ether. It is readily soluble in acetic acid, almost insoluble in chloroform, insoluble in benzene. It dissolves in caustic alkalis or alkaline carbonates with a deep red coloration, which on diluting exhibits a magnificent fluorescence, exactly resembling that of a solution of fluoresceïn itself.

III. *Metachloranthraquinone.*

Friedel and Crafts' excellent method enables us to effect various syntheses of compounds belonging to the aromatic series. In submitting a mixture of β-chlorophthalic anhydride and benzene to the action of aluminium chloride, we hoped to obtain metachlorobenzoylbenzoic acid, which might serve for the preparation of metachloranthraquinone, this substance not having been prepared hitherto.

Behr and Dorp (*Ber.*, **7**, 578) were the first to effect a similar condensation. They converted orthobenzoylbenzoic acid into anthraquinone, employing phosphoric anhydride as the condensing agent, whereas Liebermann, who used fuming sulphuric acid, obtained anthraquinonesulphonic acid. Furthermore, v. Pechmann (*Ber.*, **12**, 2126) obtained orthobromanthraquinone by heating orthobromobenzoylbenzoic acid with ordinary sulphuric acid, his method being, with slight modifications, the one we used for the preparation of metachloranthraquinone.

Metachlorobenzoylbenzoic Acid, $C_6H_3Cl(COC_6H_5)\cdot COOH$.

5 grams of fused phthalic anhydride were dissolved in 50 grams of benzene, which had been previously dried over sodium, and to the boiling solution 15 grams of aluminium chloride were gradually added. When hydrogen chloride ceased to escape, dilute hydrochloric acid was carefully added, the benzene poured off while still hot, distilled, and the residue treated for some time with a warm solu-

tion of soda. The filtrate was then acidified with hydrochloric acid, which precipitates a very greasy substance; this was again twice dissolved in soda and reprecipitated with hydrochloric acid. After dissolving the precipitate in hot acetic acid, and adding boiling water until a slight turbidity appeared, the solution was boiled with animal charcoal; on cooling, a yellowish oil and perfectly white needles were deposited, the former becoming partly crystalline after some time. To remove the oil, the product was spread on a porous plate and recrystallised from benzene: the acid was thus obtained in small brilliant crystals having the appearance of monosymmetrical prisms under the microscope.

Metachlorobenzoylbenzoic acid melts at 170°, and is readily soluble in ether, alcohol, chloroform, and acetic acid, sparingly soluble in carbon bisulphide, almost insoluble in light petroleum, whilst benzene and other aromatic hydrocarbons dissolve it only on boiling.

0·3586 gram gave 0·1955 gram AgCl.

	Calculated for $C_6H_3Cl(COC_6H_5)\cdot COOH$.	Found.
Cl........	13·63 per cent.	13·49 per cent.

Metachloranthraquinone, $C_6H_3Cl<{CO \atop CO}>C_6H_4$.

1 gram of chlorobenzoylbenzoic acid and 20 grams of pure sulphuric acid were heated for 10 minutes in an oil-bath, the temperature of which was 160—175°. The mixture was allowed to cool slowly, and then poured into water, the fine grey powder which separated being collected next day, washed well with water, and dried. It was then recrystallised twice from hot alcohol, when it was obtained in fine felted needles of a yellowish-grey colour, melting at 204°.

Metachloranthraquinone sublimes without decomposition. It is readily soluble in hot benzene, sparingly soluble in acetic acid, carbon bisulphide, or hot alcohol.

0·2783 gram gave 0·1600 gram AgCl.

	Calculated for $C_{14}H_9Cl$.	Found.
Cl........	14·64 per cent.	14·22 per cent.

IV. *Trimellitic Acid.*

This acid was discovered by Krinos (*Ber.*, **10**, 1484), Baeyer (*Ann.*, *Suppl.*, **7**, 40) shortly afterwards describing its preparation from mellitic acid. Schreder (*Annalen*, **172**, 94) then obtained it by oxidising colophony with nitric acid, and Hammerschlag (*Ber.*, **11**, 88) prepared the acid from β-alizarincarboxylic acid. In each case isophthalic was formed as a bye-product.

We tried whether Victor Meyer's method for effecting the exchange of a sulphonic group for a carboxyl-group is also applicable to β-sulphophthalic acid, and we found that trimellitic acid is formed in this way, together with some isophthalic acid.

One part of monopotassic β-sulphophthalate, and two parts of sodic formate are fused for a considerable time at a high temperature, the mass being continually stirred. During the reaction, sulphur dioxide and volatile organic sulphur compounds freely escape, and the mass gradually changes its colour from dull green to brownish-black. The melt is then softened in water, a slight excess of hydrochloric acid added, and the solution extracted with ether. The residue left on evaporating the ether is dissolved in water, ammonia added until slightly alkaline, and the solution boiled with animal charcoal. If necessary, the filtrate is once more neutralised with ammonia, and then evaporated to dryness with a slight excess of a solution of baric chloride. The residue is well washed with cold water, which dissolves the barium of isophthalate, and on decomposing this with hydrochloric acid and recrystallising the precipitate from a large quantity of boiling water, small fine needles are obtained, which melt above 300°, thus proving it to be isophthalic acid.

The residue left after the removal of the barium isophthalate by treatment with cold water is decomposed with sulphuric acid, the solution extracted with ether, the latter evaporated, and the residue dissolved in water. After neutralising it with ammonia, lead acetate is added, and the lead salt which is precipitated is decomposed with sulphuretted hydrogen. On evaporating the filtrate from the lead sulphide, trimellitic acid crystallises in small needles, united to form rosettes, and melting at 219°; when heated to a higher temperature, the anhydride distils, and separates in small oily drops, each of which on cooling solidifies in small concentrically grouped needles, melting at 158°, very characteristic of this substance.

Only 20—25 per cent. of the theoretical yield of pure trimellitic acid is obtained, this being chiefly due to the very high temperature necessary for the fusion, a considerable amount of the acid being decomposed.

The formation of trimellitic acid, the constitution of which must undoubtedly be regarded as $C_6H_3(COOH)_3$ $[(COOH)_3 = 1:2:4]$, is a further proof, if need be, that the constitution of the sulphophthalic acid employed is $C_6H_3(COOH)_2SO_3H$ $[(COOH)_2 : SO_3H = 1:2:4$.

LV.—*Mercury Sulphites, and the Constitution of Sulphites.*

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Introduction.

THE compounds described in this paper are, in formation and constitution, not ordinary salts, since they can scarcely be prepared by the ordinary process of double decomposition—that of bringing in contact a sulphite with a mercury salt having the mercury in a relation corresponding to what it is to have in the mercury sulphite. The study of these compounds should form a not unimportant part of the chapter in chemistry relating to the constitution of salts; for they are compounds of the non-saturated oxygenous radicle, SO_3, with one of that group of metals—silver, mercury, and copper—the members of which are distinguished by their inability to displace hydrogen, the relative stability of their compounds with nitrogen, sulphur, and the halogens, and their property of forming more than one series of salts in which they are strongly basic.* As such, these salts serve admirably to supply facts for the determination of the particular constitution of non-saturated oxygenous compounds.

Nothing in the properties of the sulphites of the metals had ever, we believe, been regarded as evidence that they are not dioxylic salts until notice was called to the matter by one of us in a paper read to the Society last year. When, long ago, the organic sulphites were found to be hemioxylic only, there seemed to be differences enough between them and mineral sulphites to separate them from the latter, and consequently they were made into a class called *sulphonates*, whilst the mineral sulphites were left with the dioxylic constitution attributed to them, of which some of their properties were supposed to indicate the possession. It soon became apparent, however, that this separation of the organic from the inorganic sulphites was not based upon any radical difference of constitution, for sulphite and sulphonate passed smoothly one into the other in reactions of double decomposition. The effect of recognising this has not been a happy one, as, instead of establishing anything, it appears to have unsettled the views entertained concerning the constitution of oxygenous salts, and nourished a belief that there is little that can be

* The intimate relationship of these metals, as thus defined, with the adjacent iron-platinum metals is obvious. To differentiate them from this group would hardly be in place here.

definitely said about it. Davy's theory, that oxygenous salts are binary compounds of a metallic radicle with a compound haloïd radicle, having been overthrown in the course of the development of the chemistry of carbon compounds, there has been an evident unwillingness to admit the force of facts which seem to require that this theory in a modified form should be in part reinstated. Witness in proof of this statement the efforts made to minimise the difference in basic character between the third atom of hydrogen in phosphorous acid and the other two. There can hardly be said to be any evidence, however, against certain oxygenous acids (those which are oxidisable to other acids) being partly or wholly compound haloïd acids; and all that would seem to be wanted is more evidence from inorganic sources than has as yet been brought forward in order to gain for non-saturated oxygenous acids a less reserved admission that they have a partly haloïd or non-oxylic constitution. The admission is one which seems to us pregnant with consequences, such as we indicate in another section of this paper; for it is in effect that an acid may have two kinds of basic hydrogen in consequence of constitution or structure.

Origin of Mercury Sulphites.—When it might be supposed that mercuric sulphite would be formed by direct double decomposition, it does one of three things, according to circumstances; it forms with another basylous radicle a double sulphite such as mercuric sodium sulphite or mercuric hydrogen sulphite; it forms a basic or oxysulphite with oxide of mercury taken from the nitrate or other mercuric salt; or it forms mercuroso-mercuric sulphite by suffering partial hydrolysis into sulphuric acid and its mercury element. Again, when mercurous sulphite would be expected there appears, instead, a salt metameric with it, hypomercuroso-mercuric sulphite. It is in this manner that the following mercury sulphites are formed in place of mercuric and mercurous sulphites, both unknown :—

Mercuric sodium sulphite	$Hg<\begin{matrix}SO_2{\cdot}ONa\\SO_2{\cdot}ONa\end{matrix},OH_2.$
Mercuric hydrogen sulphite ?*..	$Hg<\begin{matrix}SO_2{\cdot}OH\\SO_2{\cdot}OH\end{matrix}.$
Mercuric oxysulphite	$Hg<\begin{matrix}SO_2{\cdot}OHgO\\SO_2{\cdot}OHgO\end{matrix}>Hg,OH_2.$
Mercuric mercurous or mercurosic sulphite	$Hg<\begin{matrix}SO_2{\cdot}O\\SO_2{\cdot}O\end{matrix}>Hg_2,4OH_2.$
Mercuric hypomercurous or hypomercurosic sulphite	$Hg<\begin{matrix}SO_2{\cdot}O\\SO_2{\cdot}O\end{matrix}>Hg_3,OH_2.$

History of the Mercury Sulphites.—Mercury sulphites have already been examined by Rammelsberg, Péan de Saint-Gilles, Hirzel, Wicke,

* Known only in solution.

and A. Vogel. St.-Gilles has done most on the subject. Of the sulphites described in this paper, only mercuric sodium sulphite and mercuric oxysulphite have been previously described—both by St.-Gilles. The other sulphites of mercury described by these chemists we make out as having no existence, namely, St.-Gilles' normal mercuric sulphite, Wicke's mercurosic hydrogen sulphite, St.-Gilles' dimercuric sodium sulphite, and Rammelsberg's mercurous anhydrosulphite.

Normal Mercuric Sulphite unknown in the Separate State.

According to St.-Gilles, *normal mercuric sulphite*, $Hg''SO_3$, separates as a white, curdy precipitate, exceedingly unstable, obtained, but not in the pure state, when a syrupy solution of mercuric nitrate, free from excess of nitric acid, is treated with a dilute solution of normal sodium sulphite; either this salt, or *mercuric oxysulphite*, $(OHg_2''SO_3)_2$, or a mixture of the two, may be obtained in this way according as the mercury nitrate employed happens to be more or less basic. But, assuredly, St.-Gilles is wrong.

Mercuric Nitrate and Sodium Sulphite.—When normal mercuric nitrate, in presence of that very small amount of nitric acid which seems to be essential to its existence even in concentrated solution, is treated with a solution of normal sodium sulphite, *mercuric oxysulphite* is, from the first, precipitated in a pure or nearly pure condition, and, as a consequence, the mother-liquor proves to be much more acid than the original nitrate solution. The accumulation of this free acid soon prevents the precipitation of more oxysulphite, while much mercuric nitrate yet remains in solution. The addition of more sodium sulphite is now followed by momentary effervescence of sulphur dioxide, and a partial blackening of the white precipitate. This blackening effect was observed by St.-Gilles, and he has given, as conditions of successful preparation of the sulphite and of the oxysulphite, avoidance of excess of the precipitant and the employment of the nitrate solution in the concentrated state and the sulphite solution in the dilute state.

But when, as above described, some blackening has taken place, it soon disappears on agitating the precipitate with the mother-liquor, and, indeed, the mother-liquor may now be used to furnish more precipitate which, black at first, soon becomes white, provided too much sodium sulphite is not added. This white precipitate, however, consists not of the oxysulphite, but of another salt, *mercurosic sulphite*. Now this salt contains mercury in the proportion of only $1\frac{1}{2}$ atoms instead of 2 to 1 atom of sulphur, and its admixture with the oxysulphite in some of St.-Gilles' preparations may be the reason of his having found that the composition of the precipitate sometimes

approached that of the normal sulphite. There is another circumstance of which St.-Gilles was unaware, and which must have affected his results: the oxysulphite contains water, and is efflorescent.

The production of a basic precipitate and an acid mother-liquor by adding normal sodium sulphite to normal mercuric nitrate, settles the matter so far as concerns the supposed production of normal mercuric sulphite in this way; and a word or two on St.-Gilles' view as to the conditions which determine the composition of the precipitate is better given here than when describing the preparation of the oxysulphite. He referred the degree of basic composition of the precipitate to the degree of basic composition of the solution of nitrate used. This view of the matter depends on the supposition that nitric acid will dissolve oxide of mercury in excess of the quantity required to form the normal nitrate. It is known, however, that this property is not possessed by nitric acid; when nitric acid, sp. gr. 1·4, is treated with a paste of precipitated mercuric oxide and water, dissolution can only be carried to a certain extent before a flocculent precipitate (which is white in total absence of chloride) of basic nitrate begins to separate, and the filtered solution contains normal nitrate with a minute quantity of free acid. It is in fact impossible by any method to get a basic nitrate solution. St.-Gilles, therefore, must have got the oxysulphite just as we have done, from normal nitrate, and not, as he supposed he did, from a basic or oxynitrate.

The fact that the formation of the oxysulphite is accompanied by that of free acid is also evidence as to the non-existence of mercuric sulphite. The oxysulphite is indeed insoluble in very dilute nitric acid, and if dissolved in stronger acid it rapidly undergoes a change to mercurous sulphate. (See further the section "Mercuric Oxysulphite," p. 546.)

The substitution of a solution of *mercuric sulphate* for the nitrate is, we may assume, attended with a similar result. Mercuric oxysulphite is not, indeed, precipitated, nor perhaps could it be, because of its solubility in sulphuric acid not exceedingly dilute; this acid being necessarily present as the means of keeping the mercuric sulphate in solution. But the mixed solutions, at first clear, soon begin to deposit mercurous sulphate, which is just what happens with a solution of mercuric oxysulphite in dilute sulphuric acid. The substitution of *silver sulphite* for sodium sulphite makes no difference; the insoluble silver sulphite becomes replaced by the insoluble mercuric oxysulphite, and silver nitrate forms in the solution, together with free acid. (See "Mercuric Oxysulphite," p. 551.)

Sodium sulphite and *mercuric chloride* also fail to give mercuric sulphite, the double sulphite of mercury and sodium being formed in this case

Mercurosic Sulphite and Mercuric Chloride.—By adding mercurosic sulphite to excess of solution of mercuric chloride, there is obtained, besides mercurous chloride, what appears to be a solution of normal mercuric sulphite in mercuric chloride, if not rather one of chloride-sulphite, $Hg(SO_2OHgCl)_2$.* The solution becomes acid also, but this is accounted for by the continual decomposition of the sulphite which goes on, whereby it becomes sulphuric acid and mercurosic sulphite again; this with the mercuric chloride yields more mercurous chloride and soluble sulphite, and so on. This is the nearest approach to a solution of the normal sulphite we know of. The reaction by which it is produced is—

$$\dot{Hg}(SO_2O)_2Hg_2 + HgCl_2 = Hg(SO_2O)_2Hg + (HgCl)_2,$$

while its decomposition by hydrolysis is expressed by—

$$3Hg(SO_2O)_2Hg + 2OH_2 = 2SO_4H_2 + 2Hg(SO_2O)_2Hg_2.$$

Hypomercurosic sulphite behaves like mercurosic sulphite towards mercuric chloride.

Silver Sulphite and Mercuric Chloride.—Silver sulphite is decomposed by mercuric chloride, yielding ultimately silver chloride, mercurous chloride, and sulphuric acid:—

$$Ag_2SO_3 + OH_2 + 2HgCl_2 = 2AgCl + (HgCl)_2 + SO_4H_2.$$

A change of the mercuric chloride is thus effected in the cold which can only be accomplished by free sulphurous acid in hot solution. The primary action of silver sulphite, however, is to form mercuric sulphite or chloride-sulphite, which then suffers hydrolysis into sulphuric acid and mercurosic sulphite, from which point the decomposition proceeds as described in the section on "Mercurosic Sulphite." By pouring excess of mercuric chloride solution on to silver sulphite and quickly filtering, a solution is obtained which continues to deposit mercurous chloride for some time. The primary reaction is therefore—

$$2Ag_2SO_3 + 3HgCl_2 = 4AgCl + Hg(SO_2OHgCl)_2.$$

Sulphurous Acid and Mercuric Oxide.—Precipitated mercuric oxide can be dissolved in excess of an aqueous solution of sulphur dioxide, and can also under suitable conditions form with it an insoluble compound, mercurosic sulphite, but not normal mercuric sulphite. St.-Gilles states that when mercuric oxide in water is treated with sulphur dioxide, and the white substance produced is very quickly filtered off,

* Mercuric chloride certainly does help to keep *mercuric hydrogen sulphite* in solution (see "Mercuric Chloride and Sulphurous Acid," p. 557, in section on Mercuric Hydrogen Sulphite Solution.)

the filtrate almost immediately deposits a white precipitate which is a mixture of normal mercuric sulphite with mercurous sulphate. The precipitate obtained in this way, however, is simply mercurosic sulphite, like the white substance first produced, and is only liable to be mixed with a little mercurous sulphate when the filtrate from which it has deposited has been allowed to stand for a much longer time than that indicated by St.-Gilles.

Mercuric sodium sulphite, when treated with a little *dilute nitric acid* or sulphuric acid, yields an insoluble sulphite of mercury; this, however, is mercurosic sulphite. (See the next section.)

The only conclusion possible therefore is that mercuric sulphite has no stability, except in combination with other sulphites, or with mercuric oxide or chloride.

Mercuric Sodium Sulphite.

Our purpose has not been to include in the investigation which is the subject of this paper the double sulphites of mercury with other metals, but it would have been impossible to gain a comprehensive notion of the relations of the single sulphites, without studying the properties of at least one of the alkali double sulphites, especially as normal mercuric sulphite is unknown. Double sulphites of mercury are readily obtainable, and several of them are known. They are all mercuric salts, while the double sulphites of copper are equally all cuprous.

Mercuric sodium sulphite has already been described by St.-Gilles. Besides the ordinary sulphite, which is half of sodium and half of mercury, he has described another which is two-thirds a sulphite of mercury. The former is the subject of this section of our paper; the latter is noticed in the short section following.

Properties.—Mercuric sodium sulphite is a comparatively stable salt, colourless, crystalline, very sparingly soluble in water and neutral to litmus (St.-Gilles*). It contains water, and its composition, as ascertained by St.-Gilles, is expressed by the formula $Hg(SO_3Na)_2,OH_2$. It requires about 25 parts of cold water to dissolve it. It may be preserved for a time but little changed. It slowly turns grey, however, and decomposes into mercury, sodium sulphate, and sulphur dioxide. Heated moderately, in the dry state, it evolves much sulphur dioxide together with the water it contains; at the same time it turns brownish and greyish. When the residue is

* We write this section, like the rest of the paper, all from our own experience, except when we state otherwise, but whenever our observations are not the first recorded, we add a reference to the previous observer.

wetted, it blackens, through the formation of a flocculent, brownish-black matter, in small quantity, the principal products being metallic mercury and sodium sulphate. The brown-black matter heated with water changes into a pure black substance, insoluble in hot dilute nitric acid, and apparently sulphide. The main change effected by dry heat is probably the same as that by hot water, but a little mercuric sodium thiosulphate would seem to be also produced, by a reaction between the sulphur dioxide and some as yet undecomposed mercuric sodium sulphite. (Comp. Divers, Trans., 1885, 208.)

Heated in aqueous solution, it is converted into mercury, sulphur dioxide, and sodium sulphate :—

$$Hg(SO_3Na)_2 = Hg + SO_2 + SO_4Na_2.$$

The change is a sudden one (St.-Gilles).

According to St.-Gilles, mercurous sulphate is one of the first products of the decomposition of mercuric sodium sulphite by hot water, but blackens rapidly and then dissolves, leaving only metallic mercury. These are his equations modernised :—

$$\begin{aligned} 2Hg(SO_3Na)_2 &= Hg_2SO_4 + Na_2SO_3 + Na_2S_2O_5 \\ &= 2Hg + 2Na_2SO_4 + 2SO_2. \end{aligned}$$

We have not observed the formation of mercurous sulphate, and do not consider it possible that it could be formed. When the mercury comes out, it has a peculiar, we might say characteristic, appearance, familiar probably to many chemists; it appears as a bright rolling cloud, suggesting a precipitate of great volume, an effect due apparently to metallic reflection of light; this cloud then melts away, leaving a relatively minute, very dark grey deposit of mercury at the bottom of the vessel, the bright *mist* becomes, so to speak, a *rain* of mercury. These phenomena must have deceived St.-Gilles. Mercurous sulphate would not come out of solution from an abundance of hot acid liquid, and it cannot exist in presence of sodium sulphite, to the action of which it is exceedingly sensitive, and, therefore, would hardly be produced along with it. A single mercury sulphite when heated with water (mercuric oxide or other mercury compound being absent), becomes mercury and sulphuric acid; in the double sulphite, the sulphuric acid produced acts on the sodium sulphite, giving sodium sulphate and sulphurous acid.

The effect mentioned below of sodium hydroxide, sodium sulphite, or sodium chloride, in preventing decomposition of mercuric sodium sulphite in a hot solution, seems to show beyond doubt that the decomposition which occurs in absence of all such substances depends on the presence of acid, developed in minute quantity by the incipient decomposition of the salt. As to the sodium chloride, that

will be effective through its displacing the sulphuric acid from the sulphite by hydrochloric acid, which is incapable of causing any liberation of mercury from the double sulphite. Since acid is the cause of the change, the formation of mercurosic sulphite will precede that of free mercury. (See below.)

Sodium hydroxide is without action when in dilute solution (St.-Gilles); in its presence a solution of mercuric sodium sulphite can be boiled without decomposing. If, however, the sodium hydroxide is added in somewhat large quantity and in concentrated solution, it precipitates some of the mercuric oxide, slowly in the cold, rapidly in the hot solution. Some only of the oxide is precipitated, and this is the scarlet-red form, instead of the usual orange-yellow one. In thus yielding the *red* oxide, mercuric sodium sulphite resembles black mercuric oxychloride. *Potassium hydroxide* precipitates mercuric potassium sulphite, which is much less soluble than the sodium salt. Mercuric oxide is not precipitated from the potassium salt by the most concentrated solution of potassium hydroxide, even when hot.

Hydrochloric acid changes it into mercuric sodium chloride and sulphurous acid. *Nitric acid* (or *sulphuric acid*) sufficiently diluted, and not in great excess, yields mercurosic sulphite, sodium sulphate and nitrate, and sulphur dioxide, thus—

$$3Hg(SO_3Na)_2 + 4HNO_3 = 4NaNO_3 + Na_2SO_4 + Hg_3(SO_3)_2 + 3SO_2 + 2OH_2.$$

In this complex change, the mercuric sulphite will not be decomposed by the nitric acid itself, for dilute nitric acid does not decompose mercury sulphites. The double salt will first exchange its sodium for the hydrogen of the nitric acid, and then the mercuric hydrogen sulphite will suffer partial hydrolysis and be converted into mercurosic sulphite, sulphuric acid, and sulphurous acid, in the way described in the section on "Mercuric Hydrogen Sulphite Solution" (p. 556). The addition of a little acid to a solution of mercuric sodium sulphite makes it smell of sulphur dioxide, but does not cause immediate precipitation. Some greyish mercurosic sulphite may soon precipitate, but in any case mercury is gradually set free. The acidified solution behaves, in fact, as one of mercuric hydrogen sulphite (which see for particulars). *Sulphurous acid* is without apparent action.

Sodium sulphite, in dilute solution, is without action, but its presence stops the decomposition of mercuric sodium sulphite by heat; in concentrated solution, it precipitates much of the mercuric sodium sulphite, which is much less soluble in it than in water, slightly soluble only as it is in the latter. *Sodium chloride* solution is without action; it prevents (St.-Gilles), or almost prevents, the usual decom-

position when mercuric sodium sulphite is heated alone with water. The evaporated solution deposits crystals of the mercuric sodium sulphite unchanged, according to St.-Gilles. Sodium hydroxide has no effect on the boiling mixed solutions, indicating that there is no mercuric chloride present in the mixture. *Potassium iodide* is without action (St.-Gilles), when the sulphite is in solution. Solution of the iodide added to the solid sulphite gives a little crimson (not yellow or scarlet) precipitate, not further examined. The mother-liquor, or a mixed solution of the sulphite and iodide, gives a precipitate of ordinary mercuric iodide, when treated with sulphur dioxide (see p. 544).

Mercuric chloride solution, in the cold, is without action; but when the solutions are hot, mercurous chloride, sodium sulphate, and sulphur dioxide are produced :—

$$Cl_2Hg + Hg(SO_3Na)_2 = (ClHg)_2 + SO_4Na_2 + SO_2.$$

Or, as St.-Gilles found, hydrochloric acid may be formed (and then there will also be sulphuric acid)—

$$2OH_2 + 3Cl_2Hg + Hg(SO_3Na)_2 = 2HCl + 2(ClHg)_2 + SO_4Na_2 + SO_4H_2.$$

This occurs only when the mercuric chloride is in excess, the two acids then resulting from the well-known reaction between mercuric chloride and sulphurous acid. (St.-Gilles represents the change differently.) It is almost certain that the formation of mercurous chloride is due to the independent decomposition of the mercuric sodium sulphite, for when this is prevented by the addition of sodium chloride no change of mercuric chloride to mercurous chloride takes place. Mercurosic sulphite is formed from the mercuric sodium sulphite by the action of traces of sulphuric acid, and the mercuric chloride then acts on it, as described in the section on "Mercurosic Sulphite," to yield mercurous chloride and sulphuric acid again; so that once started, the decomposition of the sulphite proceeds very quickly. *Mercuric iodide* is without action in the cold. Heated, it is converted into the yellow iodide, and ultimately to mercurous iodide apparently. The reaction will be similar to that between the sulphite and mercuric chloride.

Mercuric oxide (precipitated) is without action in the cold, but warmed with the solution it gradually gives place to somewhat grey mercurosic sulphite, sodium sulphate being also formed. Most probably some decomposition of the mercuric sodium sulphite first occurs, as usual, into sodium sulphate, mercurosic sulphite (or mercury), and sulphurous acid, and then the sulphurous acid reacts with the mercuric oxide to form more mercurosic sulphite and sul-

phuric acid, which with sodium sulphite gives sodium sulphate and sulphurous acid, and so on.

Mercuric nitrate solution (aqueous nitric acid saturated with precipitated mercuric oxide), in excess, dissolves mercuric sodium sulphite, and then very rapidly yields a precipitate of mercuric oxysulphite. Provided the mercuric nitrate solution is somewhat concentrated (10 per cent. or stronger), and free from avoidable excess of acid, oxysulphite alone is precipitated if the mercuric sodium sulphite is added at once in quantity small enough to leave much of the nitrate undecomposed, and consequently not to generate too much nitric acid in this solution. The formation of the oxysulphite appears to be the only reaction of the mercuric nitrate itself, but other changes occur, owing to the nitric acid set at liberty:—

$$3Hg(NO_3)_2 + Hg(SO_3Na)_2 + 2OH_2 = 2NaNO_3 + 4HNO_3 + (OHg_2SO_3)_2.*$$

The mother-liquor of the oxysulphite, treated with more mercuric sodium sulphite, yields at first mercurosic sulphite, and then gradually mercurous sulphate. When the quantity of the sulphite first added to the mercuric nitrate is too great, mercurosic sulphite may or may not be precipitated, but the oxysulphite which is formed remains in solution, soon, however, to pass, with marked rise of temperature, into mercurous sulphate, which then crystallises out. In this case, it is sometimes quite practicable to pour the mother-liquor off from the mercurosic sulphite, before the mercurous sulphate begins to separate. Mercurosic sulphite can always be obtained by adding the mercuric nitrate gradually to the mercuric sodium sulphite. It is no doubt formed, in either case, through the action of the nitric acid present on the mercuric sodium sulphite, and of liberated sulphurous acid on the mercuric nitrate; whilst the mercurous sulphate is the result of a metameric change of the mercuric oxysulphite in solution in the nitric acid.

Mercurous nitrate solution precipitates mercurosic sulphite:—

$$Hg(SO_3Na)_2 + (HgNO_3)_2 = 2NaNO_3 + Hg(SO_3)_2Hg_2.$$

Mercurosic sulphite prepared in this way is always of a light buff colour, although when formed by hydrolysis it is brilliantly white. When the nitrate solution is free from nitrous acid, and, so far as possible, from nitric acid also, only traces of sulphuric acid are formed. Nitric acid, in precipitating mercurosic sulphite, generates sulphuric acid, as already explained.

* In the section on "Mercuric Oxysulphite," the nature of this remarkable reaction, and others related to it, is discussed under the heading "*Formation.*"

Mercuric sulphate solution does not precipitate mercuric oxysulphite, in consequence, apparently, of the solubility of the latter in sulphuric acid. The mixed solution soon deposits mercurous sulphate. By adding quickly about an equivalent quantity of the mercuric sodium sulphite, mercurosic sulphite can be precipitated. By adding a little *strongly* alkaline solution of mercuric sodium sulphite to excess of concentrated mercuric sulphate solution, mercuric oxysulphite can be precipitated. The mercuric sulphate solution used to prove this fact was made by saturating rather concentrated aqueous sulphuric acid with precipitated mercuric oxide, and contained only a very small quantity of free sulphuric acid.

Mercurous sulphate behaves like the nitrate, when it is shaken in the solid state with solution of mercuric sodium sulphite. It is then quickly changed to mercurosic sulphite.

Formation and Preparation.—Mercuric sodium sulphite is formed in reactions between—

(*a.*) A solution of *sodium sulphite*, or *sodium pyrosulphite* ("acid sulphite") and any *mercury sulphite*.

(*b.*) A solution of *silver sodium sulphite* and *mercuric oxysulphite*.

(*c.*) A solution of *sodium hydroxide* and any *mercury sulphite*.

(*d.*) A solution of *sodium chloride* and any *mercury sulphite*.

(*e.*) A solution of *sodium sulphite* or *pyrosulphite* and an *oxide*, or a *haloïd salt*, or an *oxylic salt*, whether *mercuric* or *mercurous*. Mercury cyanide is, however, an exception, being here inactive, although it reacts with ammonium sulphite, according to St.-Gilles. Yellow and green mercury iodides are also inactive among haloïd salts.

Concerning *a*, *b*, *c*, and *d*, consult the accounts of the several sulphites.

e. Sodium sulphite in dissolving mercuric oxide sets free sodium hydroxide. Sodium pyrosulphite and mercuric oxide yield no bye-product. Hirzel first employed mercuric oxide and a pyrosulphite for preparing mercuric ammonium sulphite. Sodium pyrosulphite and mercuric oxide afford an excellent means of preparing the double sulphite in quantity. As much heat is evolved in the reaction, it is necessary to cool, especially if the solution of sodium pyrosulphite is concentrated; if allowed to get hot, the mercuric sulphite becomes hydrolysed, yielding mercury and sulphuric acid. If excess of mercury oxide has been added, it can be dissolved by adding a little more sodium pyrosulphite. The crystalline precipitate of double sulphite can be washed with a little water and well drained. Should it contain any mercury, through the solution having been allowed to get hot, the salt can be dissolved in hot water, to which a little sodium

hydroxide has been added, and the solution filtered and set aside to crystallise, or precipitated with alcohol. When sodium sulphite is used in place of the pyrosulphite, the double sulphite is not decomposed if the solution becomes hot, and may therefore be at once drained, and then washed with alcohol, in order to remove sodium hydroxide.

Mercuric chloride is a very convenient source of the double sulphite; concentrated solution of the sulphite or pyrosulphite being poured on to the finely-powdered chloride. As it is exceedingly soluble in these solutions, no precipitation of double sulphite occurs until the sodium salt has been added in sufficient quantity. At first the salts formed are the two double salts (St.-Gilles) :—

$$2HgCl_2 + 2Na_2SO_3 = Hg(Cl_2Na)_2 + Hg(SO_3Na)_2,$$

but the further addition of sodium sulphite converts the double chloride to sodium chloride only, and brings down most of the mercury as double sulphite. If the mixture is heated when the mercury chloride is in excess, decomposition ensues (*see* "Mercuric chloride and mercuric sodium sulphite," p. 541). Sodium sulphite at once dissolves mercuric iodide as it does the chloride, but pyrosulphite has no action on it, strange to say, whilst sulphurous acid even precipitates mercuric iodide from its solution in sodium sulphite.* Mercurous chloride and mercurous oxide behave like the mercuric compounds, but half the mercury remains in the free state, the other half forming the double mercuric sulphite.

St.-Gilles found that mercuric oxide, chloride, and iodide, and mercurous chloride yielded the double sulphite. But, besides these haloïd salts, oxylic mercury salts, nitrates, and sulphates, both mercuric and mercurous, also furnish this compound; they should be added, mercuric salts especially, to the sodium salt gradually and not in excess, because in excess they destroy the double salt in the manner already described. This decomposition led St.-Gilles to believe that only haloïd salts could be used for making the double sulphites. In the case of the mercurous salts, half the mercury becomes free necessarily, but even with mercuric salts, a very little mercury, at least, is also set free; it is possible to get even half the mercury of the mercuric salt free, if the sulphite is not added in sufficient quantity for some time. The first effect of adding sodium sulphite to mercuric nitrate, for example, is to form mercuric oxysulphite and nitric acid :—

$$4Hg(NO_3)_2 + 2Na_2SO_3 + 2OH_2 = 4NaNO_3 + 4HNO_3 + (OHg_2SO_3)_2,$$

* Sulphurous acid also precipitates mercuric iodide from a solution of mercuric sodium sulphite to which potassium iodide has been added not in excess. It does not decompose mercuric sodium iodide.

and this oxysulphite dissolved in the nitric acid, or even lying in it, gradually changes to mercurous sulphate; on now adding more sodium sulphite, this mercurous sulphate yields ultimately only half its mercury as double sulphite, and half in the metallic state. By using the sodium sulphite at once in some excess, this is avoided, and almost all the mercury is converted into the double salt. The nitrates and sulphates, however, cannot be recommended for the preparation of the double salt, the oxide and chloride are far more advantageous. The formation of mercuric sodium sulphite from mercurous salts—nitrate, sulphate, chloride—is preceded by that of hypomercurosic sulphite, which is then resolved by more sodium sulphite into mercuric sodium sulphite and metallic mercury (see "Hypomercurosic Sulphite").

Chemical Composition.—We have not considered it necessary to confirm St.-Gilles' analysis of mercuric sodium sulphite; but something may be here said as to the constitution ascribed to it in this paper. If instead of $Hg{<}{\substack{SO_2ONa\\SO_2ONa}}$ mercuric sodium sulphite had the formula $Hg{<}{\substack{OSO_2Na\\SO_2ONa}}$, that is, had its mercuric radicle been half oxylic, or if it had the formula $Hg{<}{\substack{OSO_2Na\\OSO_2Na}}$, in which the mercury is represented as wholly oxylic, the cause of the relative stability of the double salts, of the non-existence of simple mercuric sulphite, and of many of the special reactions of the double salts, would cease to be apparent. There would also be no explanation why mercuric sodium sulphite has no action on litmus, and is not oxidisable by the air, whilst sodium sulphite is strongly alkaline and very oxidisable. With the constitution expressed by the formulæ $Hg(SO_2ONa)_2$ and $Na(SO_2ONa)$, sodium sulphite is alkaline, because of the instability of the non-oxylic union of sodium with sulphuryl, in presence of water, whilst in the mercuric sodium sulphite there is, through the absence of sodium so situated, the same indifference to litmus as is shown by sodium sulphate. Sodium sulphite is oxidisable, and mercuric sodium sulphite is not, because the non-oxylic sodium is oxidisable, and mercury is not; $Na(SO_3Na)$ oxidises to $NaO(SO_3Na)$, but $Hg(SO_3Na)_2$ undergoes no such change.

St.-Gilles' Dimercuric Sodium Sulphite believed not to Exist.

St.-Gilles obtains the mercuric sodium sulphite just described by adding mercuric chloride to excess of sodium sulphite, and then evaporating to crystallisation; but, as pointed out in the preceding section, by using solid mercuric chloride in powder, in place of its

very dilute cold solution, the double sulphite can be obtained, without evaporation, as a precipitate.

Besides this double sulphite, he gets another, formulated as $Hg_2Na_2(SO_3)_3,OH_2$, by employing hot saturated solutions, the mercuric chloride being in excess; some mercurous chloride is formed, which he directs should be filtered off, and the filtrate left to cool. We have, however, failed to confirm his statements. With solutions hot enough, a most abundant formation of calomel occurs, and on cooling nothing separates, except sometimes crystals of the excess of mercuric chloride. With solutions less hot, the precipitation of calomel is slow and imperfect, so that the warm filtrate continues to deposit calomel in crystals, but no new double sulphite.

St.-Gilles asserts that the solution of this double salt has an alkaline reaction. It is difficult to see why this should be so. The filtrate from the calomel which should yield this salt is markedly *acid*, as a necessary consequence of the precipitation of calomel having occurred in it. Indeed, St.-Gilles himself mentions in another place this formation of acid along with calomel (see the action of mercuric chloride on the double sulphite in preceding section, p. 541). For our own part, we can hardly conceive of any way in which such a sulphite could be formed, considering that mercuric sulphite in the separate state is unknown.

Mercuric Oxysulphite.

Mercuric oxysulphite was first obtained in 1852, by St.-Gilles, and is the only one out of the three sulphites of mercury, which have been described, the existence of which we admit.

Properties.—Mercuric oxysulphite is a curdy, or granular, dense salt, insoluble in water, and very unstable (St.-Gilles). It has a faint yellow colour, and its composition is expressed by the formula $(OHg_2SO_3)_2OH_2$. Left to itself in the air at common temperatures, it changes, in some hours, into mercurous sulphate; but in a vacuum over sulphuric acid, it can be preserved for days partly undecomposed. It is thus rendered anhydrous, but in this state consists largely of mercurous sulphate: St.-Gilles represents the salt as anhydrous when precipitated. As pointed out by him, mercuric oxysulphite (in its anhydrous state) is metameric with mercurous sulphate. In ordinary moist air, it appears to change completely into this salt, but when heated even very gradually the change is not so simple:—

$$\underset{\text{Mercuric oxysulphite.}}{Hg{<}{\begin{matrix}SO_2{\cdot}OHgO\\SO_2{\cdot}OHgO\end{matrix}}{>}Hg} = \underset{\text{Mercurous sulphate.}}{Hg_2{<}{\begin{matrix}O{\cdot}SO_2{\cdot}O\\O{\cdot}SO_2{\cdot}O\end{matrix}}{>}Hg_2.}$$

Mercuric Oxysulphite is Explosive.—This salt is remarkable in being exceedingly, though not violently, explosive. The explosion is attended by a moist, mercurial fume, the scattering of powdery particles, and by a dull sound when in a confined space. A temperature of 73° is sufficient to cause its explosion, but any quantity of it can at once be exploded at common temperatures, by touching the least portion of the whole with a heated body. It can also be exploded on the anvil, although its decomposition is so gentle that any noise produced is lost in that of the blow of the hammer. According to St.-Gilles, it is simply transformed into mercurous sulphate when heated; this salt is, indeed, the main product, but mercury and mercuric sulphate are also produced in quantity, besides water, of course, and a trace of mercuric oxysulphate. Only when slowly effected by warmth and moisture, is the change into mercurous sulphate perfect, or nearly so. It seems best to regard the decomposition of mercuric oxysulphite as being primarily, like that of the other mercury sulphites, one of hydrolysis. The first product will then be mercury, sulphuric acid, and mercuric oxide:—

$$(OHg_2SO_3)_2 + 2OH_2 = 2OHg + 2Hg + 2SO_4H_2.$$

The acid will then react with the mercuric oxide to form mercuric sulphate, and this in its turn with a portion of the mercury to form mercurous sulphate. The hydrolysis of the other sulphites of mercury to metal and acid, and of mercuric sulphate to oxide and acid, gives every probability of the correctness of the assumption here made respecting that of mercuric oxysulphite. As for the secondary union of mercury with mercuric sulphate, that can be readily effected in the cold, experimentally, in the presence of water containing very little sulphuric acid. But the mercuric oxide will also, when hot, act as an oxidising agent upon undecomposed oxysulphite, and thus determine the explosion. In proof of this, we have ascertained that a mildly explosive mixture can be made from precipitated mercuric oxide and either of the other mercury sulphites.

Water causes mercuric oxysulphite to decompose more rapidly than it does when kept dry. Heated with water it decomposes, the change being at first probably the same as when it is heated dry; but the water effects a further change, and the products are mercurous sulphate, mercuric oxysulphate, sulphuric acid, and mercury. When dissolved in aqueous solution of sulphurous acid and boiled, it decomposes in the manner which seems normal to a non-basic mercury sulphite, the sole products being mercury and sulphuric acid.

Potassium hydroxide converts it into mercuric oxide insoluble, and mercuric potassium sulphite in solution:—

$$Hg(SO_2OHgO)_2Hg + 2KOH = Hg(SO_2OK)_2 + 3HgO + H_2O.$$

Hydrochloric acid, added in excess at once, converts it into mercuric chloride and sulphurous acid. Hydrochloric acid, gradually added, causes the change of part of it into mercurosic and even hypomercurosic sulphite, by the sulphurous acid liberated from another part; more hydrochloric acid then forms mercurous chloride. If it has changed at all into mercurous sulphate, some mercurous chloride and sulphuric acid will also be produced, but sulphurous acid, even in the nascent state, has no action on mercuric chloride in the cold. If, again, it contains any of its mother-liquor of mercuric nitrate, reactions will take place on adding the hydrochloric acid, which will also produce mercurous chloride and sulphuric acid, the liberated sulphurous acid forming mercurosic sulphite from the nitrate, and the mercurosic sulphite forming mercurous chloride with the mercuric chloride. (See "Mercurosic Sulphite," p. 563.)

Nitric acid, or even *sulphuric acid*, if sufficiently dilute, hardly dissolves it, but hastens its change to mercurous sulphate. When a little more concentrated, the nitric or sulphuric acid dissolves it, *without liberating sulphur dioxide*, and then, if hydrochloric acid is added to the solution without delay, mercuric chloride and sulphur dioxide are formed in considerable quantities, besides some mercurous chloride and sulphurous acid.* But if the solution is kept for a few minutes, mercurous sulphate takes the place of the mercuric oxysulphite, and soon begins to separate. The addition of hydrochloric acid now produces only mercurous chloride and sulphuric acid. Sufficiently strong sulphuric or nitric acid liberates sulphur dioxide at once from mercuric oxysulphite.

Sulphurous acid, free or nearly free from sulphuric acid, when added in excess at once, dissolves it without forming any sulphate or sulphuric acid, and leaving mere traces of metallic mercury, the result of previous change in the oxysulphite; when, however, the sulphurous acid is added gradually, mercurosic sulphite is formed, then hypomercurosic sulphite, and, lastly, metallic mercury, as the quantity of sulphurous acid increases, while the solution from the first contains sulphuric acid, and, for a time, a little (acid) mercuric sulphite. The precipitation of mercurosic sulphite is also quickly induced when the sulphurous acid is added at once, provided it contains a good quantity of sulphuric acid. The later changes, here described, are treated of in subsequent sections of this paper; the formation of the mercurosic sulphite is represented by the equation—

$$3(OHg_2SO_3)_2 + 6SO_3H_2 = 4SO_4H_2 + 4Hg_3(SO_3)_2 + 2OH_2.$$

The effect of boiling the solution of mercuric oxysulphite in sulphurous acid has already been stated.

* Sulphuric acid can, of course, only be detected as formed, when it has not been used.

Sodium sulphite solution, added quickly in excess, dissolves it as mercuric sodium sulphite; a minute quantity of metallic mercury is left, due to the presence of a little mercurous sulphate formed by previous change of the oxysulphite. Sodium hydroxide is also formed:—

$$(OHg_2SO_3)_2 + 6Na(SO_3Na) + 2OH_2 = 4OHNa + 4Hg(SO_3Na)_2.$$

When the sodium sulphite is added gradually, however, black, flocculent hypomercurosic sulphite is first seen, which is subsequently resolved into mercury and mercuric sodium sulphite. This production of hypomercurosic sulphite seems to prove that when only partially attacked by sodium sulphite, the mercuric oxysulphite is decomposed in such a way that the basic oxide is removed, and the normal sulphite left to suffer a change practically the same as hydrolysis, but effected by the sodium hydroxide which has been formed along with it, instead of by water. Thus:—

$$2Hg(SO_2O)_2Hg_3O_2 + 8Na(SO_3Na) + 4OH_2 = 2Hg(SO_2O)Hg + 4Hg(SO_3Na)_2 + 8NaOH.$$

$$2Hg(SO_2O)_2Hg + 4NaOH = Hg(SO_2O)_2Hg_3 + 2Na_2SO_4 + 2OH_2.$$

Silver sodium sulphite solution dissolves mercuric oxysulphite, all the silver being precipitated, principally as sulphite. The precipitate is much discoloured, apparently by the presence of a little mercuric argentous sulphite (coming from mercurous sulphate). Silver oxide scarcely appears, because the original solution always contains some free sodium sulphite, and accordingly sodium hydroxide is found in solution instead.

Sodium chloride solution forms mercuric oxide, yellow and insoluble, and mercuric sodium sulphite and mercuric sodium chloride, both in solution:—

$$(OHg_2SO_3)_2 + 4NaCl = 2OHg + Hg(SO_3Na)_2 + HgCl_4Na_2.$$

A little mercurous chloride is found with the oxide, and a little sodium sulphate in the solution, owing to the mercuric oxysulphite having begun to change into mercurous sulphate by the time it is prepared for experiment.

Potassium iodide solution changes mercuric oxysulphite instantly into a dull red compound, soluble in excess of the reagent, but with much more difficulty than simple mercuric iodide, and then yielding an alkaline solution. This dull red substance is of complex nature, and consists of mercuric iodide, oxide, and sulphite, in some state of combination. Except when the solution of potassium iodide is very concentrated, the dissolution of the red compound is at once followed

by the appearance of a slight yellow precipitate convertible by a stronger solution of potassium iodide into a minute quantity of metallic mercury and dissolved mercuric iodide. The production of this yellow iodide is to be referred to the presence of some mercurous sulphate in the mercuric oxysulphite.

Mercuric chloride solution acts slowly on mercuric oxysulphite, if at all, mercurous chloride being gradually produced, together with mercuric sulphate which remains in solution with the excess of mercuric chloride. By dissolving mercuric oxysulphite in sulphuric acid before adding the mercuric chloride, the precipitation of mercurous chloride begins immediately, and proceeds rapidly until all the sulphite has been decomposed. Mercuric chloride has probably no action on mercuric oxysulphite, its action being on the mercurous sulphate into which the oxysulphite so readily changes. The action of mercuric chloride on other mercury sulphites is sharp and unmistakable, and in their case the completion of the action is retarded, instead of advanced by the presence of sulphuric acid.

Mercuric iodide, *oxide*, *nitrate*, and *sulphate*, and also *mercurous nitrate* and *sulphate* are without action. *Silver nitrate* also is without action on the oxysulphite itself, but a little silver is taken up apparently through reaction with the mercurous sulphate present.

Formation and Preparation.—Mercuric oxysulphite is formed in reactions between—

(*a.*) Solutions of *sodium sulphite* or *mercuric sodium sulphite* and *mercuric nitrate*; or solutions of *sodium sulphite* or *mercuric sodium sulphite, strongly alkaline*, and of *mercuric sulphate*.

(*b.*) *Silver sulphite* and *solution of mercuric nitrate.*

a. It was prepared first from sodium sulphite and mercuric nitrate by St.-Gilles, who states that other mercuric salts cannot be employed. In this statement he is practically correct, but by adding a strong solution of potassium or sodium hydroxide to the solution of sodium sulphite, this solution can be made to precipitate the oxysulphite from mercuric sulphate and yet leave an acid mother-liquor.

Held in acid solution, the mercuric oxysulphite soon becomes mercurous sulphate. If, without using alkali, the attempt is made to neutralise sulphuric acid by adding more sodium sulphite, mercurosic sulphite is precipitated. Mercuric oxysulphate cannot be used, as from its insolubility sodium sulphite would, for a time, be in excess in the solution.

Mercuric Nitrate and Sodium Sulphite.—Consult the account already given of the reactions between these substances, and between mercuric nitrate and mercuric sodium sulphite. The mercuric nitrate solution

should not be too dilute; St.-Gilles used even a "syrupy" solution. Such concentration is unnecessary, but there should be at least one of nitrate in ten of solution. The sodium sulphite solution is better when rather dilute; a 5 per cent. solution answers well. Both solutions should be free from chloride, otherwise mercurous chloride will be found with the oxysulphite. The sodium sulphite should be in quantity small enough to leave much mercuric nitrate undecomposed, and be added to the nitrate all at once, and with stirring. A larger yield of oxysulphite may be obtained by mixing sodium hydroxide with the sodium sulphite, but the oxysulphite is then less easily purified. The use of mercuric sodium sulphite in place of sodium sulphite is an improvement, because although it causes the liberation of as much nitric acid as the single sulphite, it generates only half as much sodium nitrate for the same quantity of oxysulphite.

Mercuric oxysulphite cannot be washed much without being rendered impure by decomposition into mercurous sulphate, and the mercuric nitrate cannot be all washed out of it by water alone, because this precipitates basic nitrate; a little nitric acid must be added to the water. Another difficulty in the way of washing the precipitate is that it is far less stable in the moist state, when mercuric nitrate is absent. The process of purifying the oxysulphite without washing by spreading it in a thin layer upon a good porous tile, has proved very satisfactory, the mother-liquor being withdrawn from it very thoroughly, and it is left as a dry, undecomposed powder, when scraped from the tile after 20 or 30 minutes (but this process is not satisfactory when, by using free alkali, mercury nitrate has been too far replaced by sodium or potassium nitrate). When well prepared, the oxysulphite should be of a pale-yellow colour, dissolve in hydrochloric acid to an almost clear solution, and be very explosive. In precipitating, it is for a moment curdy, and then becomes granular.

b. The decomposition of mercuric nitrate by silver sulphite is a very interesting fact, which depends largely, no doubt, on the relative instability of oxylic mercury salts, such as the nitrate, in comparison with the oxylic silver salt, but would seem from other evidence to be partly due also to a firmer union of sulphuryl directly with mercury than with silver: in the reaction, the silver takes the place of sodium. The silver sulphite is added to excess of the mercuric nitrate with trituration, when it is quickly replaced by mercuric oxysulphite as the insoluble matter. As is the case when sodium sulphite is used, only a part of the mercuric nitrate can be precipitated as oxysulphite; more than sufficient silver sulphite for this purpose, no doubt, produces more oxysulphite, but this now remains dissolved in the

nitric acid which has been formed, and soon becomes mercurous sulphate, which crystallises out. Prepared from silver sulphite, mercuric oxysulphite is more distinctly yellow, and always retains a very little silver,* which washing with mercuric nitrate solution does not remove. No useful quantitative analysis therefore could be made. It is highly explosive, slowly changes to mercurous sulphate, loses water on exposure, and in all respects is identical with that otherwise prepared.

Chemical Composition.—Mercuric oxysulphite is readily distinguished. Hydrochloric acid shows it to be a sulphite. Sodium hydroxide and sodium chloride both precipitate yellow mercuric oxide from it, and thus show it to be a mercuric salt and a basic compound. Hydrochloric acid also shows it not to be a mercurous salt, and, therefore, not one of the other sulphites of mercury. Its entire volatility, when previously moistened and then heated to nearly a red heat, shows the absence of alkali salt. Its great explosibility when dry is not only quite characteristic, but may be made a test of its freedom from alkali salt, which even in very small quantity greatly lessens this quality. Its gradual conversion into mercurous sulphate is evidence of its ultimate composition, and the simultaneous decrease in weight, proof of its containing water. The fume arising from its explosion also is damp. Some conversion to mercurous sulphate cannot be avoided during its preparation for analysis, but not necessarily to a greater extent than to cause its hydrochloric acid solution to be somewhat opalescent, and contain an insignificant amount of sulphate. Mercuric oxysulphite differs much in appearance from the other mercury sulphites; it is of a pale-yellow colour and forms a dense precipitate, at first curdy, then granular; hypomercurosic sulphite on the contrary is black and flocculent, whilst mercurosic sulphite forms a vividly white, voluminous, sometimes crystalline, precipitate.

By attributing to the oxysulphite a constitution in which one-fourth of its mercury is entirely in non-oxylic union with the sulphuryl, its reactions are made most capable of receiving consistent representation as well as its property of resisting the action of nitric acid (see the section on the general constitution of mercury sulphites). Although most mercuric oxysalts have three times the proportion of mercury proper to the normal salt, the oxysulphite has only twice, because it is only half an oxylic salt, and, as such, has only half as much extra base as the wholly oxylic basic salts. This is shown by

* Apparently as silver sulphate. Prepared from sodium sulphite, the oxysulphite takes up a very little silver when shaken with silver nitrate solution, and retains it during washing. Mercurous sul_hate and silver nitrate do, we find, yield silver sulphate and mercurous nitrate.

comparing the formulæ of the sulphite with that of the oxysulphate ("yellow turpeth mineral"):—

Oxysulphite.	Oxysulphate.
$Hg{<}{\genfrac{}{}{0pt}{}{SO_2{\cdot}OHgO}{SO_2{\cdot}OHgO}}{>}Hg.$	$Hg{<}{\genfrac{}{}{0pt}{}{OHgO{\cdot}SO_2{\cdot}OHgO}{OHgO{\cdot}SO_2{\cdot}OHgO}}{>}Hg.$

The results of St.-Gilles's analyses of the oxysulphite were not concordant, and led him to believe that it was mixed with more or less normal sulphite. We analysed our preparations by dissolving them in hydrochloric acid containing a little bromine, and then exposing the solution to air, without heating, until it became colourless. The sulphuric acid was precipitated first as barium salt; and then the mercury as sulphide, which was finally dried at 105—110°. Water was estimated from the loss, first in an air-pump desiccator, and then in an oven not heated above 60°. Exposure in the desiccator for 50 hours removed nearly all the water; the further exposure of 20 hours giving only an additional milligram loss. The salt now contained much sulphate, but was still explosive. Exposure to a heat of 55—60° for six hours destroyed the explosiveness of the salt, and caused a further loss of a milligram (salt taken = 0·656 gram). This loss may have been water, or it may have been mercury; we took it as the former. Heated now for six hours at 120°, it lost 2 mgrms.; this loss we regarded as mercury, and testing the residue found a little mercuric sulphate in it:—$OHg_2SO_3 = Hg + HgSO_4$. Analyses I and II were made considerably earlier than III and IV, and in very hot weather; the preparations were also exposed for a longer time on the tile. Preparations III and IV were sensibly dry, and formed non-coherent powders. Loss of water by efflorescence and by conversion to mercurous sulphate all tells on the mercury percentage number, because mercury constitutes four-fifths of the salt. III was washed with water slightly acidified with nitric acid; the others were not washed. All four were different preparations. A portion of the salt prepared for analysis IV was ignited to see to what extent it might be impure from retained bye-products; the residue amounted to 0·17 per cent.:—

	I.	II.	III.	IV*a*.	IV*b*.	$O_2Hg_4(SO_3)_2OH_2$.
Mercury ..	79·64	79·81	78·71	78·60	—	79·21
Sulphur ..	6·50	6·35	6·66	6·60	—	6·34
Oxygen ...	—	—	—	—	—	12·67
Water	—	—	—	—	1·86	1·78
						100·00

Mercuric Hydrogen Sulphite unknown in the Separate State.

Haloïd salts of mercury always give a mercuric alkali sulphite when treated with an alkali sulphite; but Wicke states that by treating solid mercuric chloride with a solution of sodium pyrosulphite he prepared mercuric hydrogen sulphite. He is certainly wrong. A solution of sodium pyrosulphite readily dissolves mercuric chloride in powder, and, if used in excess, the solution soon deposits an abundant crystalline precipitate soluble in much water. All so far is as Wicke describes it; but the precipitate, however, is mercuric sodium sulphite, and not, as he supposed it to be, mercuric hydrogen sulphite. The dissolution of the mercuric chloride liberates much sulphur dioxide, which escapes with effervescence when the solution of pyrosulphite is concentrated, as it should be, in order to precipitate the salt. There should be, of course, no liberation of sulphur dioxide if Wicke were right, nor should the crystalline salt yield a large residue of sodium sulphate on ignition as it does. Wicke's salt gave him a bright yellow basic salt when treated with potassium hydroxide. The undissolved crystals may, indeed, give a little *red* mercuric oxide with solution of *sodium* hydroxide of great concentration, but not even that with a solution of potassium hydroxide. Even if the crystals were mercuric hydrogen sulphite, they would not give a basic precipitate with potassium hydroxide, but colourless, neutral, sparingly soluble mercuric potassium sulphite. Only mercuric chloride or its compound with sodium chloride would give a bright yellow precipitate such as Wicke obtained.

What is probably a solution of mercuric hydrogen sulphite is described in the following section.

Mercuric Hydrogen Sulphite Solution.

Three chemists have published observations on the reactions of sulphur dioxide with mercuric oxide in the presence of water—Rammelsberg, Péan de St.-Gilles, and Vogel; all found a white substance take the place of the mercuric oxide, and another mercury compound go into solution, but beyond this their observations do not agree. Rammelsberg found the white substance to be a mercurous anhydrosulphite of varying composition, and the compound in solution to be mercurous sulphate. St.-Gilles states that the solution yielded a precipitate of a mixture of mercuric sulphite and mercurous sulphate, and that until this precipitate had formed it did not contain either a mercurous salt or a sulphate; whilst Vogel found the white substance to be mercurous sulphate, partly soluble in the mother-liquor as a compound not precipitable by common salt (*Watts's Dictionary; Gmelin's Handbook*).

We agree with none of these findings as a whole. We hold that neither Rammelsberg's *mercurous anhydrosulphite* nor St.-Gilles' *mercuric sulphite* exists; we find, moreover, that Vogel's white "mercurous sulphate" is really mercurosic sulphite. Coming now to the solution obtained along with the white substance, it certainly contains sulphuric acid from the very first appearance of the white substance, and St.-Gilles is wrong in denying Rammelsberg's statement to that effect. Further, it contains its mercury as mercuric salt, as St.-Gilles and Vogel (?) seem to have held, and not as mercurous salt, as Rammelsberg has stated.

None of these chemists seem to have noticed that mercuric oxide may be dissolved in sulphurous acid without the formation of any precipitate; the conditions for securing such a dissolution of the oxide are, however, simple. The sulphurous acid solution must not contain much sulphuric acid (commonly present as the result of atmospheric oxidation); and the mercuric oxide must be prepared by precipitation, must be added well divided and suspended in water to the sulphurous acid, and only in small quantity, because only a weak solution can be prepared. A solution, the same in every respect, can be obtained by using mercuric oxysulphite in place of mercuric oxide. Mercurosic sulphite and hypomercurosic sulphite can also be used in place of the oxide, but then there is a residue of metallic mercury. An impure solution can be prepared by cautiously adding, in small quantity, a solution of either mercuric nitrate or sulphate, or of mercurous nitrate or solid mercurous sulphate or mercuric oxysulphate to sulphurous acid; with mercurous salts, half the mercury separates insoluble, and with all these salts either sulphuric or nitric acid remains in the solution. Even by the action of a little nitric acid on mercuric sodium sulphite a dilute mercuric hydrogen sulphite solution can be obtained.*

Properties.—The solution reacts as one of mercuric sulphite in sulphurous acid. It is more probable that it contains mercuric acid sulphite than the normal sulphite, and may, therefore, be regarded as a solution of that salt, in absence of any evidence to the contrary. The acid sulphite is the hydrogen double salt, $Hg(SO_3H)_2$, similar to the sodium double salt, $Hg(SO_3Na)_2$, in which the mercury is wholly non-oxylic. Thus constituted, its ready conversion to mercurosic sulphite admits of more satisfactory explanation than if its mercury were half oxylic. The question as to the non-existence of acid sulphites of the alkali metals is not affected by the existence of this specially constituted mercuric salt.

* See also the account, in the latter part of this section, of the action of sulphurous acid on mercuric chloride.

Unlike the mother-liquor of mercurosic sulphite, the solution of mercuric hydrogen sulphite, when prepared from pure materials, contains no sulphuric acid, moreover, all its mercury is in mercuric combination. Alkalis give no precipitate of mercuric oxide, because they form a soluble double sulphite, precipitable, however, by alcohol. Any specific action on mercurous salts cannot be investigated, because of that exerted on them by the sulphurous acid present in the solution.

Mercuric hydrogen sulphite solution is very unstable, and readily suffers hydrolysis, either wholly or in part—wholly into mercury and sulphuric acid, in part into mercurosic sulphite and sulphuric acid—sulphurous acid remaining free in both cases. The solution deposits all its mercury slowly at common temperatures, but at once when heated, and an equivalent quantity of sulphuric acid remains in solution.* The reaction may be expressed by the equation—

$$H_2O + Hg(SO_3H)_2 = Hg + HO{\cdot}SO_3H + H{\cdot}SO_3H.$$

Partial hydrolysis, by which mercurosic sulphite is formed, is brought about in two ways. Sulphuric or nitric acid, added in small but sufficient quantity, causes it. Secondly, it is caused by adding more mercuric oxide or some mercuroxylic salt (best, a solution of mercuric nitrate or sulphate) to the solution. Whether the addition proves sufficient or not to exhaust all free sulphurous acid is a circumstance which does not affect the precipitation. Success with such different reagents renders it improbable that the hydrolysis depends on any direct reaction between them and the mercuric hydrogen sulphite. The explanation we offer of the change is that it is induced by effecting a state of supersaturation of the solution with mercuric hydrogen sulphite, so that partial hydrolysis occurs and mercurosic sulphite is precipitated. Mercury sulphites are insoluble in dilute nitric or sulphuric acid, and therefore the addition of one of these acids brings about the state of supersaturation which leads to the sudden hydrolysis and precipitation. Mercuric oxide or salts generate more acid sulphite in the solution, and in this way cause supersaturation. According to this explanation, mercuric hydrogen sulphite must be regarded as a salt soluble in a large quantity of water, and hydrolysed by less water.

The result of the hydrolysis of mercuric hydrogen sulphite when it has only proceeded to the extent of separating one-third of the sulphur as sulphuric acid, appears to depend on the difference between oxylic and non-oxylic mercury compounds; the mercuric radicle, Hg, alone can hold the non-oxylic position in a sulphite, the

* Facts also mentioned by Vogel; but the solution he examined had been produced along with the white substance (mercurosic sulphite), and already therefore contained sulphuric acid.

mercurous radicle, Hg_2, cannot. The mercurous radicle, on the other hand, can hold the oxylic position, provided a mercuric radicle is in non-oxylic relation to the sulphuryl, whilst the mercuric radicle cannot do so, except in the partial and complex way seen in the basic mercuric oxysulphite. Accordingly, the conversion of mercuric hydrogen sulphite to mercurosic sulphite may be represented by the following equation, in which the upper line shows the hydrolysis of a third of the sulphite, and the lower the double decomposition whereby, with the assistance of mercury set free by hydrolysis, two molecules of mercury hydrogen sulphite become mercury sulphite and hydrogen sulphite :—

$$\left.\begin{array}{l} Hg''(SO_3H)_2 + OH_2 \\ Hg''(SO_3H)_2 + Hg''(SO_3H)_2 \end{array}\right\} = \left\{\begin{array}{l} H{\cdot}SO_3H + HO{\cdot}SO_3H \\ 2H{\cdot}SO_3H + Hg''(SO_3)_2Hg'_2. \end{array}\right.$$

Mercuric Chloride and Sulphurous Acid.—It is well known that a nearly boiling solution of mercuric chloride is converted by a stream of sulphur dioxide into mercurous chloride, hydrochloric acid, and sulphuric acid. This reaction does not take place at all in the cold, but the two substances are, even then, not indifferent to each other.

Mercuric chloride is very much more soluble in sulphurous acid than in water. The solution on exposure to air rapidly crusts over and also deposits much crystalline precipitate, both consisting of mercuric chloride rendered insoluble by the escape of some of the sulphur dioxide. Mercuric chloride loses its greater solubility in sulphurous acid if much *sulphuric acid* is present, so that the addition of dilute sulphuric acid to the sulphurous solution quickly induces crystallisation of mercuric chloride. When saturated with mercuric chloride, sulphurous acid dissolves much more *mercuric oxide* than it can otherwise do, without yielding an immediate precipitate. Either on standing or on addition of sufficient mercuric oxide, precipitation begins and slowly proceeds, the precipitate being crystalline mercurous chloride. The appearance of this is equivalent to that of mercurosic sulphite, for, as is described in the next section, this sulphite and mercuric chloride at once react yielding mercurous chloride and mercuric sulphite. Sulphuric acid is formed along with the mercurosic sulphite. That the solution slowly decomposes, even when not fully saturated with mercuric oxide, may be accounted for by regarding a solution of mercuric chloride in sulphurous acid as being charged with mercuric hydrogen sulphite, formed by decomposition of some of the mercuric chloride:—

$$HgCl_2 + 2H(SO_3H) = Hg(SO_3H)_2 + 2HCl.$$

As such it will, by dissolving mercuric oxide, become supersaturated with mercuric hydrogen sulphite, through the action of the oxide on

the free sulphurous acid, even though still more oxide may be soluble in it, on account of the hydrochloric acid present. Mercuric chloride is also much more soluble in a solution of sodium sulphite or pyrosulphite, and is then certainly converted into mercuric sodium sulphite.

In further support of the belief, expressed in the last paragraph, that mercuric chloride and sulphurous acid partly change into mercuric hydrogen sulphite and hydrochloric acid, it may be pointed out that, according to Sartorious, it is only between 70° and 80°, and in dilute solutions, that mercuric chloride is completely precipitated as mercurous chloride by sulphurous acid: for, in the first place, it is just at that temperature that mercury sulphites suffer hydrolysis, mercuric sulphite then passing into the stage of mercurosic sulphite, from which mercurous chloride would be precipitated by the hydrochloric acid; and, in the second place, too concentrated a solution of mercuric chloride would, in the course of precipitation, charge the water with so much sulphuric acid that it would stop the conversion of the remainder of the mercuric chloride into sulphite, and therefore into mercurous chloride. The action of sodium sulphite on mercuric chloride also supports the above view, for here the precipitation of the mercurous chloride by heat is certainly preceded by the formation of mercuric sodium sulphite (see the sections on "Normal Mercuric Sulphite and Mercuric Sodium Sulphite").

It may be startling to hear of sulphurous acid decomposing mercuric chloride, when sulphuric acid cannot do so, but then it must be remembered that sulphurous acid completely decomposes both the mercury sulphates, as well as the nitrates, into sulphites and free acid.

Mercurous Chloride and Sulphurous Acid.—According to Vogel, mercurous chloride is converted by sulphurous acid into a grey substance, probably a subchloride; we find the action to be exceedingly slight, however. Ordinary calomel becomes a little greyish when suspended in a small quantity of water through which sulphur dioxide is passed; the effect is soon produced, and does not increase during continued contact with the gas: only traces of hydrochloric acid are to be found in the mother-liquor; there are also traces of sulphuric acid, but these would soon be formed in any case in the solution of sulphurous acid. Left for a day in old solution of sulphurous acid, calomel became dark grey, although even then the action was but slight, for very little hydrochloric acid was in solution. In this case, the sulphuric acid which had accumulated in the solution, probably assisted by rendering the calomel slightly soluble. Precipitated mercurous chloride becomes coloured more readily in water containing sulphurous acid, but still only light grey

and with the formation of mere traces of hydrochloric acid. The difficulty of getting precipitated mercurous chloride quite free from other salts makes this slight reaction of little significance. We doubt whether there is any reaction at all between true mercurous chloride and sulphurous acid. When mercurous chloride is precipitated by sulphurous acid itself, it is of dazzling whiteness, which is a strange fact, if it is discoloured by sulphurous acid in other cases. (For an account of the behaviour of mercurous chloride with sodium sulphite, see the section on "Hypomercurosic Sulphite," p. 572.)

Mercurosic Sulphite.

Mercurosic sulphite was in the hands of both Rammelsberg and St.-Gilles, without its true nature being recognised by either of them. It is here, for the first time, therefore, described at any length, and with the composition we give to it. It is a well-defined salt, although from its history it might be supposed not to be such.

Properties.—Mercurosic sulphite is obtained in somewhat different states. Prepared by adding mercuric oxide to sulphurous acid solution, it is in lustrous, crystalline particles, which form felted sheets like paper, when drained on a tile till dry. Prepared from a paste of mercuric oxide and gaseous sulphur dioxide, it is not visibly crystalline, but it forms a voluminous precipitate of crystalline habit, is brilliantly white, and, when pressed whilst moist, crepitates like starch. Prepared by reaction between another mercury sulphite and a mercury nitrate or sulphate, it is a voluminous, apparently amorphous precipitate, of a buff colour. It is then not quite pure, indeed, but its colour can hardly be referred to the presence of any coloured impurity. Since mercurous chloride occurs both of a fine white colour and of a pale buff, it seems allowable to hold that mercurosic sulphite may also do so. We have not got the buff-coloured variety free enough from sulphate, for useful quantitative analysis, but its qualitative reactions are those of the white mercurosic sulphite.

Mercurosic sulphite is insoluble in water. Its composition is expressed by the formula $Hg_3(SO_3)_2(OH_2)_4$. It is very efflorescent, and becomes anhydrous in the desiccator. Only when it is crystalline can it be obtained dry, with all the water of composition retained. Rammelsberg found in his red, crystalline cuprosic (or "cuprosocupric") sulphite 2 mols. H_2O, and St.-Gilles in his yellow amorphous cuprosic sulphite, 5 mols. H_2O. Our preparations of mercurosic sulphite, air-dried in hot weather, have shown slightly less than 2 mols. H_2O, and we cannot be certain that our preparation having 4 mols. H_2O had not already effloresced, and lost a fifth mol. H_2O, although we believe it had not.

Mercurosic sulphite is so stable when dry as to be but very little changed after long keeping. In a closed vessel, it gradually darkens in colour, but nearly bleaches again on exposure to the air for some time. The darkening is in all probability due to the formation of a little hypomercurosic sulphite. Slowly in the air, more quickly in a vacuum, it acquires a slight permanent grey colour, due to the presence of a minute quantity of mercury. The slow decomposition of mercurosic sulphate results in the production of mercurous sulphate, metallic mercury, sulphur dioxide, and water, the same products as those produced by heat. Sulphurous acid blackens both mercurous sulphate and mercurosic sulphite by forming hypomercurosic sulphite; hence, no doubt, the partial blackening when the mercurosic sulphite is kept shut up. After blackening and bleaching in the air, the changed sulphite may be somewhat buff-coloured.

Heated dry at a temperature of about 80°, it evolves sulphur dioxide, mercury, and water, and becomes at first black, then grey-white, leaving mercurous sulphate and some of the mercury as a residue; these may be separated by further heating, so as to volatilise the mercury. The blackening may certainly be referred to the formation of hypomercurosic sulphite, and although it is for the time very great, it is only transitory if the heat is maintained. Examined when blackest, the amount of undecomposed sulphite proves to be exceedingly small. It is not probable that hypomercurosic sulphite forms an intermediate product in the decomposition of the mercurosic sulphite; the moist sulphur dioxide no doubt produces it by a secondary action on the undecomposed mercurosic sulphite, or on the mercurous sulphate (see "Hypomercurosic Sulphite," p. 571). The decomposition of mercurosic sulphite by heat is represented by the equations—

$$Hg_3(SO_3)_2 + 2OH_2 = 3Hg + 2SO_4H_2.$$
$$Hg + Hg_3(SO_3)_2 + 2SO_4H_2 = 2Hg_2SO_4 + 2SO_2 + 2OH_2.$$

Some quantitative measurements of this reaction have sometimes proved in close agreement with the equation, and never widely different from it. We have got 61·2, 58·4, 56·1, and 61·9 per cent. of mercurous sulphate. With 2 mols. H_2O retained by the salt used, the calculated number is 62·3 per cent.; with 4 mols. H_2O nearly 60 per cent. The sulphur dioxide was also measured, but as the gas was not dried, the results were only rough approximations. Instead of 8 per cent., 8·6, 7·8, 8·5, and 8·1 were found. The experiments were made with the aid of the Sprengel pump. There are two material sources of loss of mercurous sulphate in such an experiment; the mercurous sulphate is apt to be lost as fume; and the hydrolysis of the sulphite is liable to proceed more rapidly than the action on the remaining

sulphite of the sulphuric acid generated by the hydrolysis. A low production of sulphate should be more evident when the water is as much as 4 mols., and this probably accounts for our getting such a low number as 56 per cent. in one case.

Heated with water, it is converted tumultuously into metal and sulphuric acid.* Enough water being present, no mercurous sulphate is produced :—

$$Hg_3(SO_3)_2 + 2OH_2 = 3Hg + 2SO_4H_2.$$

When the salt is heated dry, its decomposition begins in all probability in this way, but is then modified by the reaction between the sulphuric acid and unchanged sulphite, giving mercurous sulphate and sulphurous acid. The non-production of any mercuric sulphate is to be expected, as it is easy to show experimentally the instant conversion of mercuric sulphate to mercurous sulphate by moist mercury.

Potassium hydroxide converts it into mercurous oxide, insoluble, and mercuric potassium sulphite, going into solution—

$$Hg(SO_3)_2Hg_2 + 2KOH = OH_2 + OHg_2 + Hg(SO_3K)_2,$$

the potassium displacing the mercurous but leaving the mercuric radicle.†

Hydrochloric acid at once decomposes it, the products being sulphurous acid and the two chlorides of mercury. When the mercurosic sulphite is buff-coloured, the mercurous chloride from it is of the same colour. No sulphuric acid is produced in this reaction. The preparations of buff-coloured sulphite, however, to start with, always contain a small quantity of sulphate. *Nitric acid and sulphuric acid* in the dilute state are without action on mercurosic sulphite. Stronger acids dissolve it, but the nitric acid scarcely before being strong enough to oxidise the sulphite. *Sulphurous acid* blackens

* The property was observed by Rammelsberg in what he regarded as mercurous anhydrosulphite, which he prepared in the same way as is here given for preparing mercurosic sulphite.

† Rammelsberg, by similar treatment of the salt prepared by him, obtained very little potassium sulphite. He would seem to have been working then with a preparation mostly mercurous sulphate. According to Watts (*Watts's Dictionary*) he found his salt to "oxidise" rapidly to mercurous sulphate, mercury becoming free. It is material to state that mercury sulphites do not *oxidise* at all: they do become sulphates, but not by uniting with atmospheric oxygen. It is further to be remarked that the salt, viewed as either mercurous anhydrosulphite or mercurosic sulphite, could not well yield metallic mercury in becoming mercurous sulphate by oxidation, because it already contains less than two atoms of mercury to one of sulphur. It is rightly stated to yield mercury by changing into mercurous sulphate, but it does so in the way mentioned in the text.

and decomposes it, dissolving out the elements of mercuric sulphite and leaving hypomercurosic sulphite insoluble for a time, but then also decomposing (see section on "Hypomercurosic Sulphite," p. 567). The presence of sulphuric or nitric acid greatly hinders, and for a time at least altogether prevents the action of the sulphurous acid, a circumstance greatly facilitating the preparation of mercurosic sulphite. The influence of these acids is important, not only in preserving mercurosic sulphite, but also in connection with its production (see the section on "Mercuric Hydrogen Sulphite Solution," p. 554).

The reaction between sulphurous acid and mercurosic sulphite in absence of sulphuric acid, consists in the exchange of non-oxylic hydrogen for oxylic mercury, as expressed in the following equation:—

$$2Hg(SO_3)_2Hg_2 + 2H(SO_3H) = Hg(SO_3)_2Hg_3 + 2Hg(SO_3H)_2.$$

Sodium sulphite solution produces effects similar to those of sulphurous acid, but acts more rapidly than the acid. The mercurosic sulphite is blackened by being converted into hypomercurosic sulphite insoluble, and mercuric sodium sulphite dissolving; here also as with sulphurous acid, the sodium sulphite exchanges its non-oxylic sodium for half the mercury of the oxylic mercurous radicle of the mercurosic sulphite, the other half of this mercury going to form hypomercurosic sulphite with mercurosic sulphite:—

$$2Hg(SO_3)_2Hg_2 + 2Na(SO_3Na) = Hg(SO_3)_2Hg_3 + 2Hg(SO_3Na)_2.$$

The hypomercurosic sulphite thus formed is acted on by more sodium sulphite, becoming mercuric sodium sulphite and free mercury (see the section on "Hypomercurosic Sulphite," p. 569). *Silver sodium sulphite* solution yields mercuric sodium sulphite in solution, all the silver being precipitated if not in excess. The insoluble sulphite is very black, and appears to be a mercury silver sulphite; it is too black for hypomercurosic sulphite, even unmixed with white silver sulphite;* besides, hypomercurosic sulphite at once reacts with silver sodium sulphite. The reaction between the silver sodium sulphite and mercurosic sulphite appears, then, to be expressed by the equation—

$$Hg(SO_3)_2Hg_2 + 4Ag(SO_3Na) = 2Hg(SO_3)_2Ag_4 + 2Hg(SO_3Na)_2,$$

in which mercuric argentous sulphite appears.

Sodium chloride solution added freely produces much black hypomercurosic sulphite, which slowly disappears on digestion. By add-

* The "silver sulphide" observed by Vogel, and again by Pleischl, to be formed by the action of sulphurous acid and sulphites upon silver salts, must have been argentous sulphite, and not sulphide at all.

ing the sodium chloride gradually, hypomercurosic sulphite is only produced by the first portions. This difference is due to the mercury salts which go into solution by the action of the first portions modifying that of those added afterwards. The final result of the addition of sodium chloride is expressed by the equation—

$$Hg(SO_3)_2Hg_2 + 2NaCl = Hg(SO_3Na)_2 + (HgCl)_2,$$

but the primary action appears to be that of an exchange of sodium for the oxylic mercury, in which only half of this mercury combines with the chlorine, the other half then going to unite with more mercurosic sulphite—

$$2Hg(SO_3)_2Hg_2 + 4NaCl = Hg(SO_3Na)_2 + Hg(SO_3)_2Hg_3 + HgCl_4Na_2.$$

Then, as the quantity of mercuric chloride increases, and the mercurosic sulphite becomes less, all the mercury goes to form mercurous chloride, while any hypomercurosic sulphite previously formed is slowly converted into chloride (see the section on "Hypomercurosic Sulphite"). *Mercuric sodium chloride* acts in the same way as sodium chloride, the mercuric chloride taking no part; it has no action of its own on mercurosic sulphite, but when sodium chloride is present this salt acts first. *Mercuric chloride* solution added, not in excess, produces mercurous chloride and sulphuric acid, all the mercury being precipitated—

$$Hg_3(SO_3)_2 + 2OH_2 + 3HgCl_2 = 3(HgCl)_2 + 2SO_4H_2;$$

but if added at once in excess, much mercuric sulphite goes into solution in the mercuric chloride, and then slowly changes to mercurous chloride and sulphuric acid, as already described under *normal mercuric sulphite. Potassium iodide* solution forms a brownish-yellow mercury iodide and a solution of mercuric potassium sulphite. *Mercuric iodide, oxide, nitrate,* and *sulphate,* and *mercurous nitrate* and *sulphate,* are without action.

Formation and Preparation.—Mercurosic sulphite is formed in reactions between—

(*a.*) *Sulphurous acid,* water, and *mercuric oxide;*
(*b.*) *Sulphurous acid,* water, and *mercuric oxysulphite;*
(*c.*) *Sulphurous acid,* water, and either *mercuric oxysulphate* or solution of *mercuric nitrate,* or solution of *mercuric sulphate;*
(*d.*) *Mercuric sodium sulphite* and either dilute *nitric acid* or dilute *sulphuric acid* (solutions of either *sodium sulphite* or *mercuric sodium sulphite,* and either *mercuric nitrate* or *mercuric sulphate*);

(*e.*) A *warm* solution of *mercuric sodium sulphite* and *mercuric oxide;*

(*f.*) *Mercuric sodium sulphite* and either *mercurous sulphate* or a solution of *mercurous nitrate;*

(*g.*) *Hypomercurosic sulphite* and a solution of either *mercuric nitrate* or *mercuric sulphate.*

a. (I.) Precipitated mercuric oxide made into a thick paste with water is treated with a stream of sulphur dioxide in a vessel immersed in cold water; the paste rapidly thins by dissolution of the oxide, mercurosic sulphite being formed, and gradually increasing in quantity. In this action, the oxide goes through the stage of soluble sulphite in changing into mercurosic sulphite. Excess of sulphur dioxide does no harm. If the mixture is allowed to grow hot, or if too much water has been taken, there will be some blackening of the product during the passage of the gas, due to the formation of hypomercurosic sulphite; there will be blackening also if water is afterwards added to the sulphite and its mother-liquor. The reason of this is that the permanence of the mercurosic sulphite in presence of sulphurous acid is conditional on there being enough sulphuric acid in the solution; this is a bye-product of the reaction, and the addition of water acts injuriously by diluting this acid too much. Just at first, in the preparation, before any sulphuric acid is formed, the sulphurous acid is at once absorbed by the abundant mercuric oxide; at this period of the operation, however, blackening occurs readily, and the vessel should be well agitated until enough sulphuric acid has been generated. Although the mercurosic sulphite can generally be washed with strongly acidulated water without turning grey, it is better to drain the sulphite on a good porous tile; in half an hour or so it will be found to be dry, surprisingly free from sulphuric acid, pulverulent and non-coherent when scraped off the tile, and almost pure.

(II.) Precipitated mercuric oxide in paste is treated with sulphurous acid solution containing a moderate quantity of sulphuric acid. This method of preparation yields the crystalline variety of the sulphite. When drained dry on the tile, it forms glistening paper-like laminæ. It is possible to prepare mercurosic sulphite without blackening it, by the use of sulphurous acid unmixed with sulphuric acid; to ensure success, the mercuric oxide should be in thick paste, and the sulphurous acid concentrated and added gradually with stirring and cooling.

b. Mercuric oxysulphite may be used instead of mercuric oxide in the preceding method of preparation.

c. Mercuric oxysulphate may also be used in place of mercuric

oxide in method *a*. Solution of mercuric nitrate, with the least sufficient excess of nitric acid, is a very convenient source of (crystalline) mercurosic sulphite, when treated with sulphur dioxide, either gaseous or in solution. A solution of mercuric sulphate, not too acid, may also be taken.

d. Mercuric sodium sulphite and nitric or sulphuric acid. The sulphite is best used in the solid state, and the suitable quantity of acid added at once. Insufficient acid causes blackening. The reaction is discussed in the section on "Mercuric Sodium Sulphite" (p. 549). Mercuric sodium sulphite and mercuric nitrate form mercurosic sulphite only by secondary reactions due to the nitric acid (see the section on "Mercuric Sodium Sulphite"). Sodium sulphite and mercuric nitrate first form mercuric sodium sulphite and sodium nitrate, and then the mercuric sodium sulphite reacts with more mercuric nitrate. Were it not for the free acid of the mercuric nitrate solution, it should be possible to add the nitrate until all sodium sulphite had become mercuric sodium sulphite, and after that, further addition of nitrate would form mercuric oxysulphite. But the quantity of free acid sufficient to start the formation of mercurosic sulphite is very small, and (neglecting to account for this) the following equation serves to express the result of the change in presence of acid :—

$$3Hg(NO_3)_2 + 3Na_2SO_3 + OH_2 = Hg_3(SO_3)_2 + Na_2SO_4 + 4NaNO_3 + 2HNO_3.$$

e. Mercuric sodium sulphite and mercuric oxide react together as described in the section on this sulphite.

f. Mercuric sodium sulphite and mercurous nitrate yield the buff-coloured variety of mercurosic sulphite.

g. Hypomercurosic sulphite digested in a solution of mercuric nitrate (or sulphate) quickly changes to the buff-coloured variety of mercurosic sulphite. Hypomercurosic sulphite, as prepared, is nearly always mixed with metallic mercury, but this does not remain in the mercurosic sulphite prepared from it, as mercury is remarkably soluble in mercuric nitrate solution.

Chemical Composition.—The action of hydrochloric acid clearly shows mercurosic sulphite to be a sulphite, and both a mercuric and mercurous salt. The mercurous chloride produced could not come from the mercuric chloride because sulphurous acid has no reducing action upon it in the cold. It could indeed be formed by using an insufficient quantity of hydrochloric acid at first, when the sulphurous acid would act on the remaining mercurosic sulphite (supposed here wholly mercuric) and generate hypomercurosic sulphite, which with more hydrochloric acid would give mercurous chloride; but the suggestion of any

such action is precluded by the fact that no sulphuric acid is formed by the hydrochloric acid. Further, potassium hydroxide gives mercurous oxide; and sodium chloride gives mercurous chloride. The mercuric chloride formed in abundance by hydrochloric acid, without liberation of mercury, is full proof of its mercuric nature. Not only is it easily distinguished from mercurous sulphate, by yielding mercuric chloride and sulphur dioxide, and not sulphuric acid, but also at once by decomposing in boiling water, not to yield a yellow residue nearly as large as itself, but only grey mercury of exceedingly small volume. Moreover, its appearance is characteristic. The presence of water in it is readily detected by heating it in a tube. The representation of mercurosic sulphite as having one-third of its mercury in non-oxylic union with the sulphuryl, or as having the mercuric and not the mercurous radicle so related is in full agreement with its reactions.

Sulphur and mercury were determined in the usual way, as already described in the section on "Mercuric Oxysulphite." Water was estimated by drying in a vacuum over sulphuric acid; a few hours proved sufficient to remove nearly all the water, but the time in the desiccator was from 20 to 40 hours. A crystalline preparation showed 4 mols. H_2O, but other preparations showed less. These had to be longer on the tile to get them dry, and loss of water by efflorescence took place; efflorescence proceeds so rapidly as to make the salt show loss of weight during the operation of weighing.

I. 0·8005 gram taken for the mercury, and 0·8110 gram for the sulphur determination.

II. 1·4955 grams taken for water.

III. 1·2533 grams taken for water.

IV. 1·2808 grams taken for water, and of the dried salt, 1·1413 grams for sulphur and nercury. All four quantities were taken from separate preparations.

	$1\frac{1}{2}H_2O$.	I.	II.	III.	IV.	$Hg_3(SO_3)_2,4H_2O$.
Mercury ..	76·24	75·94	—	—	72·20	72·12
Sulphur ..	8·13	8·27	—	—	8·04	7·69
Oxygen ...	12·20	—	—	—	—	11·54
Water	3·43	—	3·21	5·03	8·59	8·65
	100·00					100·00

Rammelsberg's Mercurous Anhydrosulphite believed not to Exist.

Rammelsberg states that the mercury sulphite obtained by him, by treating mercuric oxide with sulphur dioxide in the presence of water, had the composition of a mercurous anhydrosulphite—either $(Hg_2SO_3)_2SO_2$ or $(Hg_2SO_3)_3SO_2$. His results are neither very definite

nor theoretically very probable, and therefore as we have failed to get in this way any other sulphite than mercurosic sulphite in the solid state—a salt neither anhydrous nor exclusively mercurous—we are convinced that he must, from some cause, have mistaken the nature and composition of the product he obtained.

Hypomercurosic Sulphite.

Oxygenous mercurous salts are blackened by sulphurous acid and soluble sulphites; they are then converted into hypomercurosic sulphite, a well-defined salt, which has hitherto escaped recognition. It was mistaken by Vogel for mercury, notwithstanding its black colour.

Properties.—Hypomercurosic sulphite is a greyish-black amorphous substance, obtained as a voluminous, flocculent precipitate, insoluble in water. It is very unstable in water, but can be preserved dry for a considerable time, without much change. Its composition is expressed by the formula $Hg_4(SO_3)_2OH_2$. Left to itself at common temperatures, it very slowly evolves sulphur dioxide, leaving mercurous sulphate and mercury. The co-operation of moisture is, no doubt, essential to this change, the primary form of which will be hydrolysis into mercury and sulphuric acid, to be followed by reaction between unchanged sulphite and the sulphuric acid. The production of sulphur dioxide and mercury shows the change not to be one of oxidation of sulphite to sulphate by the air. The equation of the change is—

$$Hg_4(SO_3)_2OH_2 = 2Hg + Hg_2SO_4 + SO_2 + OH_2.$$

Heated dry, to a temperature of about 80°, it rapidly undergoes the same change as that which takes place slowly in the air. On heating it gradually in a vacuum, so as to volatilise the liberated mercury, weights of mercurous sulphate were obtained equal to 46·90 per cent. in one case, and 49·86 per cent. in another, calculation requiring 50·72 per cent. for $Hg_4(SO_3)_2OH_2$. These results are satisfactory, when it is considered that sulphuric acid may be carried off with the mercury and water vapour, without acting on the remaining sulphite, the decomposition being a rapid one; and, further, that in consequence of previous hydrolysis during the operation of getting the sulphite dry for use, a little mercury is liable to be already present with the prepared sulphite.

Heated with sufficient water, it is rapidly and tumultuously converted into metal and sulphuric acid:—

$$Hg_4(SO_3)_2OH_2 + OH_2 = 4Hg + 2SO_4H_2.$$

If the proportion of water is so small as to leave the sulphuric acid somewhat concentrated, some mercurous sulphate is also formed, but not otherwise. The production of the sulphate is then due to reaction between unchanged sulphite and the sulphuric acid. We must anticipate here, in order to say in explanation that hypomercurosic sulphite resists the action of rather dilute sulphuric acid. We made an estimation of the mercury and sulphuric acid produced by the hydrolysis of the sulphite, by weighing the former directly and the latter as barium salt. The results, although not obtained under the best conditions, may be given; they were:—Mercury, 82·33 per cent., instead of 81·80; sulphur, 5·23 per cent., instead of 6·54.

Potassium hydroxide solution converts it into mercuric potassium sulphite, which dissolves, and mercurous oxide and mercury which remain insoluble. The decomposition of the sulphite by alkali is expressed by the equation—

$$Hg(SO_2O)_2Hg_3,OH_2 + 2KOH = Hg(SO_2OK)_2,OH_2 + Hg + Hg_2O + OH_2.$$

Hydrochloric acid at once liberates sulphur dioxide, and forms mercuric chloride in some quantity. The insoluble matter only slowly changes from the nearly black colour of the sulphite to a light grey, even with thorough trituration of the whole in a mortar. It then consists of mercurous chloride and a very little free mercury, while the solution contains no more than minute quantities of mercuric chloride. The primary reaction is evidently expressed by the equation—

$$Hg(SO_3)_2Hg_3 + 4HCl = HgCl_2 + 2H_2SO_3 + Hg + (HgCl)_2.$$

The mercury and the mercuric chloride then slowly unite and form more mercurous chloride, as they can be shown experimentally to have the power to do. Possibly a black hypomercurous chloride, Hg_3Cl_2, is one of the primary products, and then acts upon the mercuric chloride:—

$$Hg_3Cl_2 + HgCl_2 = 2(HgCl)_2.$$

Nitric acid and *sulphuric acid*, when dilute, have no action. It only reacts with nitric acid when that acid is strong enough to oxidise it. Its resistance to acids is very striking, and furnishes a ready means of quickly distinguishing it from mercurous oxide. Acid solutions of mercurous salts are instantly precipitated by sulphur dioxide, gaseous, or in solution. *Sulphurous acid* solution decomposes it, producing a solution of mercuric hydrogen sulphite, and a residue of mercury:—

$$Hg(SO_3)_2Hg_3 + 2H(SO_3H) = 2Hg + 2Hg(SO_3H)_2.$$

There is here double decomposition, in which mercury in the oxylic position exchanges with hydrogen into the non-oxylic one. Two-thirds of this oxylic mercury become free, however, because only *mercuric* hydrogen sulphite can exist. The action of sulphurous acid on hypomercurosic sulphite is almost entirely prevented by the presence of some sulphuric acid; but for this, the sulphite could not be prepared in a state at all approaching purity. The same is true of mercurosic sulphite.

Sodium sulphite solution converts it into mercuric sodium sulphite dissolving, and a residue of mercury, the action being similar to that of sulphurous acid. *Silver sodium sulphite* solution takes mercury in place of its silver, all the silver being precipitated, if not in excess. The blackish hypomercurosic sulphite is converted into something still blacker, probably mercuric argentous sulphite. Excess of silver sodium sulphite does not destroy this black matter, or only slowly destroys it. If boiled with water, it yields spongy silver amalgam; and when washed with cold water, it slowly undergoes the same change. The reaction is perhaps—

$$Hg(SO_3)_2Hg_3 + 6Ag(SO_3Na) = Hg(SO_3)_2Ag_4 + 2Ag + 3Hg(SO_3Na)_2.$$

If the silver sodium sulphite is used in excess, and after the reaction, it is diluted with water, it shows a greyish-white turbidity, through the liberation of a minute quantity of silver. Apparently, a very little mercuric argentous sulphite dissolves in the undiluted solution of the other sulphites, and on dilution parts with some of its silver.

Sodium chloride solution produces mercurous chloride, mercuric sodium sulphite, and mercury:—

$$Hg(SO_3)_2Hg_3 + 2NaCl = Hg(SO_3Na)_2 + Hg + (HgCl)_2.$$

Potassium iodide solution converts it into mercurous iodide and potassium sulphite. Then, as in any case would happen, concentrated solution of potassium iodide resolves this mercurous iodide into mercury, and mercuric iodide dissolving as double iodide; but the presence of the potassium sulphite does not appear to affect this decomposition of the mercurous iodide. As stated in the section on mercuric sodium sulphite, alkali sulphites do not act on mercurous iodide as they do on mercurous chloride and mercuric iodide.

Mercuric chloride solution reacts with hypomercurosic sulphite to form mercurous chloride and sulphuric acid:—

$$Hg_4(SO_3)_2 + 2OH_2 + 4HgCl_2 = 2SO_4H_2 + 4(HgCl)_2,$$

but its action takes some time to complete, and the mercurous chloride

is at first very grey. When the mercuric chloride is not in excess, the filtered solution of sulphuric acid is free from both mercury and chlorine, but when it is added quickly in excess and at once filtered, a solution is obtained which continues to deposit crystalline mercurous chloride for some time. The reaction is, therefore, similar to that between mercurosic sulphite and mercuric chloride. First, mercuric sulphite (or chloride sulphite) and hypomercurous chloride (or mercury and mercurous chloride) are formed:—

$$Hg(SO_3)_2Hg_3 + HgCl_2 = Hg(SO_3)_2Hg + Hg_3Cl_2(?Hg + Hg_2Cl_2);$$

then mercuric sulphite and water become mercurosic sulphite and sulphuric acid; the mercurosic sulphite decomposes with mercuric chloride, as stated in describing that sulphite; and so the changes follow on until no more sulphite remains. The hypomercurous chloride (or mercury) slowly unites with mercuric chloride to form mercurous chloride, according to the equation given in this section in the paragraph on the action of hydrochloric acid.

Mercuric oxide (precipitated) has no immediate action on moist hypomercurosic sulphite. With the oxide not in excess, the mixture slowly changes to mercurous sulphate and mercury, a result apparently not due to any direct reaction between the two substances. With the oxide in excess, we once got a bright orange-brown mercury oxysulphite; this has not been fully examined. It is at once decomposed by hydrochloric acid in the usual way, but is insoluble in dilute nitric acid; this affords a ready means of removing the excess of mercuric oxide. A little mercurous sulphate was present with it. *Mercuric nitrate* solution rapidly converts it into mercurosic sulphite, becoming itself changed to mercurous nitrate:—

$$Hg(SO_3)_2Hg_3 + Hg(NO_3)_2 = Hg(SO_3)_2Hg_2 + (HgNO_3)_2.$$

As mercuric nitrate readily takes up mercury, the above equation, showing the transfer of one of the three atoms of the hypomercurous radicle to the mercuric nitrate, presents no difficulty. The mercurosic sulphite obtained in this way is always of a light buff colour, instead of white. This colour is characteristic of mercurosic sulphite not obtained by hydrolytic decomposition; for the reaction between mercuric sodium sulphite and mercurous nitrate or sulphate yields it also of this colour. Formed by hydrolytic methods, it is always exceedingly white. *Mercuric sulphate* solution behaves like mercuric nitrate, but in this case the mercurous sulphate formed precipitates and mixes with the mercurosic sulphite. *Mercurous nitrate* solution and *mercurous sulphate* are, as might be expected, inactive. So, too, is *silver nitrate*.

Formation and Preparation.—Hypomercurosic sulphite is formed in reactions between—

(*a.*) *Sulphurous acid*, water, and *mercurosic sulphite* (also *mercuric oxysulphite*);
(*b.*) *Sulphurous acid*, water, and *mercurous sulphate*, or solution of *mercurous nitrate*;
(*c.*) Solution of *sodium sulphite* and *mercuric oxysulphite*;
(*d.*) Solution of *sodium sulphite* and *mercurosic sulphite*;
(*e.*) Solution of *sodium sulphite* and *mercurous sulphate*, or solution of *mercurous nitrate* or *mercurous chloride*;
(*f.*) *Silver sulphite* and solution of *mercurous nitrate* or *mercurous sulphate* in water.

a. Mercurosic sulphite, when treated with sulphurous acid, yields two-thirds of its mercury as hypomercurosic sulphite, the rest dissolving as mercuric acid sulphite. Since mercuric oxysulphite with sulphurous acid yields mercurosic sulphite, it also yields hypomercurosic sulphite. The sulphurous acid must be added to these sulphites gradually and not in excess, as otherwise it will decompose the hypomercurosic sulphite. The blackening of mercurosic sulphite when heated appears to be a case of the reaction between sulphurous acid and mercurosic sulphite.

b. Mercurous sulphate and nitrate are at once decomposed by sulphurous acid, even in presence of dilute sulphuric or nitric acid, into hypomercurosic sulphite and their respective acids. As the mercurous radicle, from the nitrate, cannot hold the non-oxylic relation to sulphuryl, half its mercury goes to form the hypomercurous radicle on the oxylic side:—

$$2(H{\cdot}SO_3H) + 2(HgNO_3)_2 = Hg(SO_3)_2Hg_3 + 4HNO_3.$$

As already mentioned, hypomercurosic sulphite is destroyed, as well as formed, by sulphurous acid, but its destruction takes place only when the solution contains an inufficient quantity of either sulphuric or nitric acid. In preparing the sulphite by this method, the sulphurous acid solution should be mixed with a little sulphuric acid before pouring it into the mercurous nitrate solution or on to the sulphate. Mercurous sulphate and sulphurous acid mixed with a little sulphuric acid, are the best source of hypomercurosic sulphite. The sulphate should not be dense and crystallised, but flocculent, as obtained by precipitation; in presence of sulphuric acid, the sulphurous acid may be added to it in excess. If concentrated sulphurous acid is added gradually and with stirring to the mercurous sulphate in the state of paste, the sulphuric acid can be dispensed with, but as soon as the sulphurous acid is in slight excess, further addition of it must be

stopped; it liberates enough sulphuric acid to protect the hypomercurosic sulphite from its further action, provided an excess of it does not too much *dilute* this sulphuric acid; it is safer and simpler, however, to add some sulphuric acid to the sulphurous acid. It is better not to attempt to purify the sulphite by much washing, as it begins at once to suffer hydrolysis by treatment with water; draining in a thin layer on a good porous tile is the best way, and leaves mere traces of sulphuric acid. The preparation must not be grey, even when dry, but almost black, and in the moist state must not be clotted; clotting and grey colour are proof of hydrolysis having proceeded to some extent.

c. The formation of hypomercurosic sulphite from mercuric oxysulphite by sodium sulphite is somewhat obscure in nature, and has already been described. The amount of hypomercurosic sulphite produced is proportionately small, but is certainly not dependent on the presence of mercurous sulphate before addition of the sodium sulphite.

d. The conversion of mercurosic sulphite to hypomercurosic sulphite by sodium sulphite is quite similar to that which happens when sulphurous acid is used. The sodium sulphite must not be added in excess.

e. Sodium sulphite added to either moist mercurous sulphate or a solution of mercurous nitrate, produces its effect by double decomposition, but as the mercurous radicle cannot hold the non-oxylic position in a sulphite, half its mercury is left to unite with the oxylic mercurous radicle, and convert it into the hypomercurous radicle:—

$$2Na(SO_2ONa) + 2(HgNO_3)_2 = Hg(SO_2O)_2Hg_3 + 4NaNO_3.$$

The sodium sulphate solution should be dilute and be added gradually, but not in excess, as it then rapidly attacks the hypomercurosic sulphite. It is difficult, however, to avoid having a temporary excess of the sodium sulphite, particularly when working with mercurous sulphate; and the process is, therefore, very inferior to that in which sulphurous acid is used, if a nearly pure sulphite is desired. In the case of mercurous chloride, it is hardly possible to go nearer to success than seeing the blackening effect of the sulphide upon the chloride.

f. Silver sulphite can be used effectively as a means of producing hypomercurosic sulphite from mercurous nitrate and even from mercurous sulphate. The insolubility of silver sulphite is so great that it can remain for a few moments in the solution of mercurous nitrate before beginning to lose its whiteness; when started, however, the change proceeds rapidly and soon becomes complete if the mercurous

nitrate is in excess. In working with mercurous sulphate, the two salts require intimate trituration with water for some time. The blackening that occurs shows how fully they act on each other, but the hypomercurosic sulphite and silver sulphate can, of course, not be separated. The reaction between mercurosic sulphite and silver sodium sulphite has already been described.

Chemical Composition.—Although hypomercurosic sulphite is produced by the reaction between other sulphites and mercurous salts, its behaviour with reagents shows that it is not a mercurous salt, for it always yields a mercuric compound, as well as mercury and a mercurous compound. Its reactions with hydrochloric acid and with mercuric chloride seem to leave its constitution as a mercuric hypomercurous salt beyond doubt. The mercuric chloride and mercury formed in this case, if well shaken together, combine almost completely and become mercurous chloride.

That in its formation from mercurous nitrate or sulphate, the mercury of two mercurous radicles becomes distributed as a mercuric and a hypomercurous radicle, is in agreement with what takes place on adding excess of sodium or hydrogen sulphate, as then mercuric sodium or hydrogen sulphite and mercury are the products. Evidence of the existence of other hypomercurous compounds is not altogether wanting. Mercury shaken with mercuric chloride solution yields a nearly black precipitate, which is slowly converted into white mercurous chloride by contact with more mercuric chloride. Finely divided mercury is, of course, far removed from black in colour, but if, in spite of this, it should be contended that the black substance may be mercury only, it will be enough, perhaps, to point out for reply that Vogel mistook hypomercurosic sulphite for *mercury in the state of a black-grey powder* (*Gmelin's Handbook*, 6), when he saw it produced by the action of sulphurous acid on mercurous nitrate.

The reactions of hypomercurosic sulphite are clearly those of a sulphite. Heated in a tube it yields water. Its insolubility in dilute nitric acid at once distinguishes it from mercurous oxide. Its colour distinguishes it from other mercury sulphites, and also from grey lustrous mercury, into which it so quickly changes, under conditions similar to those in which it is formed. From mercury it is also distinguished in being flocculent and voluminous. Its behaviour, when heated, either wet or dry, has already been described as evidence of its quantitative composition.

Dissolved in a mixture of bromine and hydrochloric acid, and precipitated by the usual methods, it has given us the quantities of mercury and sulphur tabulated below. Water has not been directly determined, because sulphur dioxide is also evolved in the desiccator.

The weights taken for analysis were 0·8073 and 1·2510 grams of different preparations.

	I.	II.	$Hg_4(SO_3)_2,OH_2$.
Mercury	81·55	81·95	81·80
Sulphur	6·50	6·44	6·54
Oxygen........	—	—	9·82
Water	—	—	1·84
			100·00

General Constitution of the Mercury-Sulphites.

The reactions, formation, and composition of the mercury sulphites seem to establish the five propositions which follow concerning their general constitution.

1. In mercury sulphites, the relation of basic to acid radicle is of two kinds; it is half like that of the basic element in oxylic salts (such as sulphates and nitrates), and half like that of the basic element in salts of the halogens, including cyanogen.

2. The mercuric radicle, Hg, takes up and preserves the non-oxylic relation to sulphuryl, with an energy to be compared to that it exerts in its cyanide and iodide. This is the central conception in the chemistry of the mercury sulphites, for without it all peculiarities stand unexplained.

3. The mercurous radicle, Hg_2, never holds non-oxylic relation with sulphuryl, and when presented in chemical reactions to a sulphite, resolves itself into the mercuric radicle which goes to the sulphuryl, and mercury which becomes free or changed into the hypomercurous radicle, Hg_3.

4. The mercuric radicle, in presence of water, can hold the oxylic relation to sulphuryl in such an imperfect way only, that two-thirds of it are in combination with simple oxygen radicles. But two such compounds are known, both of which have exclusively the mercuric radicle for base, namely, mercuric oxysulphite and mercuric oxysulphate :—

Oxysulphite.	Oxysulphate.
$Hg{<}{\begin{matrix}SO_2{\cdot}OHgO\\SO_2{\cdot}OHgO\end{matrix}}{>}Hg$	$Hg{<}{\begin{matrix}OHgO{\cdot}SO_2{\cdot}OHgO\\OHgO{\cdot}SO_2{\cdot}OHgO\end{matrix}}{>}Hg.$

The oxysulphite presents itself as a combination at once stable and unstable; for while its formation actually involves the liberation of nitric acid from a nitrate, as well as its insolubility in this acid when dilute, yet it is afterwards exceedingly liable to decomposition. Its formation in circumstances, the like of which would prevent that of any other basic salt, seems due to the energy with which the mercuric

radicle and sulphuryl enter into non-oxylic union, the sulphuryl being then compelled to take up other mercuric radicles on its oxylic side, in order to complete the salt. It is the feeble hold of sulphuryl on the mercuric radicles in oxylic union with it, which then, in conjunction with the readiness of the sulphites of mercury and of silver to undergo hydrolysis, gives to this sulphite its great instability.

5. The mercurous radicle can enter into oxylic union with sulphuryl, but only when this is exclusively united with mercury as base. Mercuroso-mercuric sulphite and mercurous sulphate are, therefore, the only mercurous salts, no double mercurous sulphates being known:—

Mercurosic sulphite. $$Hg{<}{\begin{matrix}SO_2{\cdot}O\\SO_2{\cdot}O\end{matrix}}{>}Hg_2$$

Mercurous sulphate. $$Hg{<}{\begin{matrix}O{\cdot}SO_2{\cdot}O\\O{\cdot}SO_2{\cdot}O\end{matrix}}{>}Hg_2.$$

The Nature of Reduction by Means of Sulphurous Acid.

In describing the formation and changes of mercury sulphites, most of what we wish to say about the reduction of mercuric to mercurous salt, and of the latter to metal by sulphurous acid, has already in a manner been said. The subject is, however, of such interest and importance, and the nature and course of the reduction has hitherto been so superficially or so erroneously apprehended, that a section of this paper may well be devoted to giving a connected statement of what we have made out about it.

When sulphurous acid or a sulphite effects the reduction of mercury or silver, or reduces ferric to ferrous salts, thereby becoming sulphuric acid or sulphate, *it is not really the case that the sulphurous acid is, as such or directly, oxidised by the metallic salts*, either immediately, or, in the case of haloïd salts, through the intervention of water. As an expression of the result of heating sulphurous acid with mercuric chloride, the following equation is of course true, and for its purpose is free from objection:—

$$H_2SO_3 + OH_2 + HgCl_2 = H_2SO_4 + 2HCl + Hg.$$

But it is wrong if the implication is intended that the sulphurous acid and the mercuric chloride make a combined attack upon water, and share its elements between them, the truth being that they first attack each other (see the section on "Mercuric Hydrogen Sulphite").

In most cases certainly, and probably in all, the first step in the reduction is the formation of a sulphite of the metal with its combining value undiminished. Mercuric salts yield mercuric hydrogen sulphite, mercuric sodium sulphite or other double salt, mercuric oxysulphite, or mercuric sulphite combined with chloride. According to

Berzelius, mercuric selenite and sulphurous acid become mercurous selenite and sulphuric acid, but this is a mistake, the sulphurous acid displaces the selenious acid, and the mercuric sulphite suffers hydrolysis into mercurosic sulphite and sulphuric acid. With excess of sulphurous acid, the selenium is slowly precipitated from solution and colours the mercurosic sulphite, thus making it look a reducing selenite and liable to cause a mistake: mercurous selenite is not formed. Mercurous sulphite is unknown, but mercurous salts yield hypomercurosic sulphite metameric with it (see the previous section). Silver nitrate, sulphate, chloride, or oxide, treated with sodium sulphite become either silver sulphite or silver sodium sulphite, and the nitrate and sulphate become sulphite when treated with sulphurous acid. The reddening of ferric solutions on the addition of sulphurous acid as well as of sodium sulphite, precedes reduction, and this indicates the formation of ferric sulphite, for a similarly coloured solution is obtained by dissolving ferric hydroxide in sulphurous acid, and this has the properties of a solution of ferric sulphite. Dilute sulphuric acid or nitric acid does not prevent the formation of sulphites; and when from the presence of one of these acids in greater concentration this formation is prevented, so also is reduction. Sulphurous acid has scarcely any action on mercurous or silver chloride, perhaps none if sulphuric acid and other impurities are altogether absent; so that here, too, absence of reduction goes with non-formation of sulphite. It does reduce mercuric chloride, and here apparently also forms sulphite (see section on "Mercuric Hydrogen Sulphite").

A sulphite being formed, metal becomes reduced from it in one of two ways. Mercurosic and hypomercurosic sulphites treated with sulphurous acid or sodium sulphite are resolved into free mercury and mercuric sulphite, dissolving as double salt of hydrogen or sodium. The consequence is remarkable, for it follows from this that mercury may become metal without oxidation of any sulphurous acid or sulphite radicle whatever; thus (ignoring the intermediate formation of hypomercurosic sulphite) the reaction between mercurous chloride (or nitrate) and sodium sulphite, and that between mercurous nitrate and sulphurous acid are expressed by the equations—

$$(HgCl)_2 + 2Na(SO_3Na) = Hg + Hg(SO_3Na)_2 + 2NaCl$$
$$(HgNO_3)_2 + 2H(SO_3H) = Hg + Hg(SO_3H)_2 + 2HNO_3.$$

Such reactions can hardly be regarded as cases of reduction, half the metal drops out in the interaction of the substances, just as it does when potassium iodide acts on mercurous iodide. They might, with as little impropriety, be treated as cases of *oxidation* by a sulphite, since a mercuric is got from a mercurous salt.

The other way in which reduction of metal is brought about is by

hydrolysis, or an equivalent change. Water converts the sulphite into metal and sulphuric acid. The hydrolysis proceeds in stages, usually apparent:—

$$6Hg_2(SO_3)_2 + 4OH_2 = 4Hg_3(SO_3)_2 + 4SO_4H_2$$
$$4Hg_3(SO_3)_2 + 2OH_2 = 3Hg_4(SO_3)_2 + 2SO_4H_2$$
$$3Hg_4(SO_3)_2 + 6OH_2 = 12Hg + 6SO_4H_2.$$

But this is unimportant here, since the stages are alike in the nature of the reduction, and the reactions of the several sulphites may be said to prove that mercury each time becomes free, but then unites with unchanged salt so as to build up the mercurous and hypomercurous radicles. Ferric sulphite apparently does not suffer hydrolysis, but still it becomes reduced to ferrous sulphite by the iron losing one-third of its hold upon the sulphite radicle. There is nearly the same separation between metal and sulphite radicle as occurs when mercuric sulphite becomes mercurosic sulphite by hydrolysis, but the acid radicle is differently disposed of. According to Gélis, the red solution of ferric hydroxide in sulphurous acid is a solution of ferric sulphite, and slowly suffers, in absence of other acid or of air, conversion into ferrous sulphite and ferrous hyposulphate.

But ferrous hyposulphate is equivalent to ferrous sulphite combined with sulphuric oxide, and when boiled with an acid it yields sulphate; in this way the ferric sulphite becomes ferrous sulphite and sulphuric acid.

Hydrolysis therefore is equivalent to oxidation of sulphurous acid to sulphuric acid by reduction of mercury, silver, or ferric compounds; but in nature it is the displacement of metal by the hydrogen and hydroxyl of water, in which process hydrogen takes the place of the metal, and oxygen converts its half haloïd into wholly oxylic union with the sulphuryl. It will be seen that reduction by hydrolysis of the sulphites is a process the reverse of that of the separation of metal by the action of sodium or hydrogen sulphite. In the latter, mercurous becomes mercuric salt by part of the mercury dropping out of combination with the sulphite radicle; in the former, when part only of the sulphite radicle is separated from the mercury of the water, mercuric becomes partly mercurous or hypomercurous salt.

The Oxidation and Hydrolysis of Sulphites as Evidence of their Constitution.

Mercury and silver sulphites are not liable to atmospheric oxidation. In this respect, they resemble organic sulphites (sulphonates), and differ from most inorganic ones. There seems no reason why they

should be so if sulphites are dioxylic salts of thionyl, $(AgO)_2SO$; but when sulphites are regarded as having a hemi-haloïd constitution, the explanation at once suggests itself.

In forming a sulphite with sulphur dioxide, a basic oxide becomes half deoxidised, just as it does when it unites with chlorine, except that with this it gives a haloïd salt and an oxylic salt, whereas with sulphur dioxide it gives but one salt, hemi-haloïd, hemi-oxylic, because here, simply, the acid radicle is bivalent. Thus conceived, a sulphite possessing, as it does, half-deoxidised metal, is liable to direct oxidation according as its metal is readily oxidisable or not. The ready hydrolysis of the sulphites not liable to oxidation serves to show that sulphuryl prefers dioxylic union with metallic radicles to the half-haloïd union with them it has in sulphites; it is therefore ready in all sulphites for union with more oxygen, but when the sulphite is of mercury or silver it cannot directly* take up oxygen because of the indifference of the metal.

Chlorides, to which in illustration reference has just been made, do not oxidise, because their haloïd radicle has a characteristic preference for direct or non-oxylic union with metals; their basic radicle, however, does in some cases oxidise at elevated temperatures, their chlorine then becoming free. (This aspect of varying oxidisability of haloïd salts is further noticed in the section on the "Relation of Selenites to Sulphites.")

On the assumption that sulphites are thionyl compounds, there is no way of accounting for the hydrolysis of some of them. Water would have to be decomposed by the sulphite into its elements, its oxygen going to the thionyl, and its hydrogen taking up oxygen again (!) by displacing mercury or silver; or the sulphite would have first to be changed by hydrolysis into basic oxide and sulphurous acid or oxide, and then the latter act reducingly on the basic oxide. Neither of these interpretations of the nature of the change is probable. It will therefore be sufficient to point out again, in connection with the second, that on trial sulphurous acid does not become oxidised by mercury oxide, but combines with it to form a mercuric sulphite. Hydrolysis may be regarded as a test of the constitution of an oxygenous salt; if it yields acid and basic oxide, or hydroxide, the

* "Directly," that is, as regards the argument in the text, although Traube's view of atmospheric oxidation is most likely true here, as in other cases:

$$\left.\begin{matrix}Na\\NaO_3S\end{matrix}\right\} + OH_2 + O_2 = \left.\begin{matrix}Na\\NaO_3S\end{matrix}\right\}O + H_2O_2.$$

In the report of the Inventions Exhibition by the editor of the *Journal of the Society of Chemical Industry*, Messrs. Boake and Co. are said to have exhibited potassium metasulphite (pyrosulphite) having the advantage of not being liable to oxidation. This property will of course be lost in presence of moisture.

salt is wholly oxylic; if it yields acid and metal (hydrogen or hydrocarbon), the salt is partly haloïd.

Sulphites resemble Chlorides, Iodides, and Cyanides in Properties.

Mercury and silver sulphites possess certain properties which are of value as indications of the partly haloïd character of their acid radicle, because they belong more or less fully to haloïd as distinguished from oxylic salts. Such properties are, that of decomposing in ways equivalent to a separation of the metal from the salt radicle; relative insolubility in acids; and that of forming double salts when possible.

Silver and Mercury Sulphites Decompose much in the same way as some Haloïd Salts.—Mercuric sulphite is unlike any purely oxylic salt, and resembles many haloïd salts, in yielding up a third or a half of its chlorous radicle, and thus becoming mercurosic or hypomercurosic sulphite. Thus, manganese tetrachloride becomes a lower chloride by giving up a quarter or a half of its chlorine; cupric and ferric iodides become cuprous and ferrous by setting free some of their iodine; cupric cyanide becomes cuprous by parting with cyanogen, and so in other cases. Again, much as these sulphites become metal and sulphuric oxide in hot water, gold chlorides by a moderate heat become metal and chlorine. The differentiation of a sulphite from a purely oxylic salt is here perfect, and although its resemblance to a simple haloïd salt is not complete, the conditions of its decomposition being unlike those of a haloïd in including the presence and activity of water, there is good reason for this in the consideration that the sulphite is half oxylic in constitution, and consequently requires the assistance of water in decomposing.

The Comparative Insolubility of Silver and Mercury Sulphites in Acids.—Before trying to show the significance of this fact, it may be well to point out, more distinctly than is done in Gmelin's or other handbooks, the extent of the insolubility of silver sulphite.

Silver nitrate solution is copiously precipitated by sulphurous acid. The reaction is immediate, and so certain that silver nitrate solution proves as sensitive to either gaseous or dissolved sulphur dioxide as lime-water is to carbon dioxide, whilst the brilliant whiteness of the silver sulphite makes the effect much more visible than the lime-water effect, and thus well fitted for class demonstrations, and as a test for sulphur dioxide. Except when the silver nitrate is in concentrated solution, the precipitation of silver is almost complete. Nitric acid is, of course, liberated in this reaction, and so insoluble is silver sulphite in this acid as to be hardly affected until the acid is strong enough to oxidise it and become itself reduced to nitrous fumes. Excess of sulphurous acid has no action on the precipitate, for a time at any rate, in presence of the nitric acid which has been set free.

Silver sulphate is quickly converted by sulphurous acid into silver sulphite and sulphuric acid. On the other hand, sufficiently concentrated or hot dilute sulphuric acid decomposes the sulphite, reversing the change.

The great insolubility of mercurosic and, above all, hypomercurosic sulphite, in nitric acid, and even sulphuric acid, is noticed in other sections of this paper; and so is the behaviour of mercuric oxysulphite towards acids, but this it will be well to describe again in the present connection because of its significance. Although a basic salt it, like the other sulphites, is insoluble in rather dilute acids, as might indeed be expected from the fact of its formation being attended with liberation of nitric acid. When it does dissolve in stronger acid, it does so with little or no liberation of sulphur dioxide; the solution, indeed, changes rapidly, and mercurous sulphate is the result, but if, without delay, hydrochloric acid is added to the solution, very little mercurous chloride is precipitated, and abundance of sulphur dioxide is given off—effects which show that the sulphite *dissolves as such*. Hence it will be seen that the insolubility of mercury and silver sulphites is not, in some way or other, a *cause* of their not being decomposed by acids, but a *result* rather of their resisting decomposition.

To come now to the interpretation of this resistance of silver and mercury sulphites to the action of oxylic acids, as evidence that sulphites have the character of haloïd salts. In the first place, if these sulphites were simply oxylic salts they would be the only oxylic salts of silver and mercury insoluble in dilute nitric acid, the sulphates in part excepted; while as haloïd salts they are far from exceptional in this respect. Stronger acids decompose them, and so does strong sulphuric acid decompose, to some extent, mercury haloïd salts. The action of nitric acid on silver sulphite is the same as on silver cyanide (except that it is more easily exerted than on the latter), these salts being unchanged by cold dilute acid, and decomposed with deoxidation of the nitric acid when this is hot and strong.

In the second place, if sulphites had to be ranked simply as oxylic salts, it would be incomprehensible that silver and mercury sulphites should be insoluble in dilute *sulphuric* acid, and be freely formed from the *sulphates* by sulphurous acid. For sulphurous acid not only proves to be much weaker than sulphuric acid in salts of other metals, but as the elements of the two acids are the same, the acid with more oxygen should be the stronger acid. As haloïd salts, on the other hand, silver and mercury sulphites are not peculiar, since, as every one knows, not only do the strong haloïd acids decompose silver and mercury sulphates, but so also does hydrogen cyanide, feeble as it is towards alkalis. Sulphites, as haloïd salts, have an essentially

different constitution from that of sulphates, half their metal being directly united to the sulphur of sulphuryl; so that mercury and silver sulphites form and exist in the presence of sulphuric acid, for much the same reason that mercury mercaptide proves to be a very stable body, although mercury ethoxide cannot even exist.

The Stability of the Double Sulphites resembles that of the Double Cyanides, Iodides, and Chlorides.—A reference to the section on "Mercuric Sodium Sulphite" will show how this salt resembles the corresponding iodide and cyanide, in the circumstances under which it forms, and in its behaviour to reagents. Silver sodium sulphite is but little behind the mercury salt in this respect. Sodium hydroxide and chloride do not precipitate the silver from the double salt, whilst silver oxide, chloride, and other salts of silver dissolve in sodium sulphite.* The double sulphites, like the double cyanides, are neutral to litmus, although alkali cyanides and sulphites are strongly alkaline.

Plainly in the matter of forming double salts, sulphates resemble haloïd salts. Many oxylic salts do indeed form double salts, but not under such conditions as those in which the mercury and silver double sulphites can form. These wholly oxylic double salts are able to resist little more than the action of water, and appear to be held together mainly by forces of crystallisation only. Such salts of mercury and silver are but little known, and are decomposable even by water.

In the same way that sulphites resemble haloïd salts they are like thiosulphates, in which also the metal is half oxylic—$AgS{\cdot}SO_2{\cdot}ONa$. Hyposulphates, so closely related to sulphites in origin, show no relation to haloïd salts; they are wholly oxylic—$(SO_2ONa)_2$.

The Constitution of Sulphites a Clue to that of Cyanides and other Halides.

The simple halogens, and cyanogen, like the radicle of the sulphites, form double salts of a little oxidisable metal and a highly oxidisable metal, which are more stable than their salts, formed exclusively of one or the other kind of metal. It seems clear that this two-sided character of the sulphite radicle in its combination with metals is due to its constitution, through which it acts half as an oxylic radicle. But, this being the case, the halogens should owe their two-sided character as acid radicles also to peculiarities of constitution. Cyanogen is a compound radicle, and admits of being dealt with from this point of view. Chemists are not decided as to whether

* This was pointed out in a previous paper by one of us last year. Captain Abney has recently recommended the use in photography of sodium sulphite, in place of thiosulphate.

cyanides are carbamines or nitriles; more commonly they are represented as the latter, but there is much to be said in favour of their being carbamines, as pointed out by one of us in a previous paper (Trans., 1885, 227). Now by giving them a constitution half-carbamine, half-nitrile, an explanation is afforded of their remarkable tendency to be double salts. Writing them thus—

Potassium cyanide.	Silver potassium cyanide.
$KN \vdots C \vdots N \vdots CK$	$AgN \vdots C \vdots N \vdots CK$,

with half their metal united to nitrogen and half to carbon, it would seem certain that silver or mercury, from its affinity for nitrogen, would form a more stable combination than potassium on the nitrogen side of the cyanogen, and will not do so on the carbon side.

The stability of mercury potassium iodide is no less remarkable than that of the cyanide or sulphite, although in it the chlorous radicle is a simple halogen. When hydrogen iodide is put in contact with a mixture of potassium hydroxide and mercuric oxide, it does not take one and leave the other, but satisfies itself half with one and half with the other. It would, therefore, seem that in $Hg(I_2K)_2$, the group I_2(or I_4) has a structure, constitution, or internal relation of parts, by which it presents to basic radicles two forms of combining power. Why should it not? Turning to a kindred matter, well before the attention of chemists, we will reply by another question. Which, we would ask, is more probable: that the resemblance of the periodic series of the elements to the homologous and isologous series of organic compounds is a chance one; or that it is due to the elements being themselves complexes?

Note on the Constitution of Fulminates, by Edward Divers.—It will be seen that the matter of the section to which this note is appended, bears on the question as to the nature of the fulminates, since they show so marked a difference in their two units of basicity. I hope yet to publish again on their formation and constitution, as some work now going on in my laboratory, on mercury and nitric acid, promises to throw light on the matter; but in the present connection I wish to point out a modification of the formula I have proposed for a fulminate, which, without much altering its general significance, would make it fulfil two desirable ends. Instead of $AgO\overline{CNONC}Ag$, I would write $AgOCNO\underset{Ag}{N}C$, that is, remove Ag from C to an N, disconnect the Cs, and read the Cs and Ns with valencies the same as they have in carbamines, either C'' and N''' or C^{IV} and N^{V}. Thus, first, the advantage is gained of representing the carbons disconnected, in accordance with the evidence afforded by the action of

chlorine and iodine on the fulminates (Trans., 1885, 78), that fulminates do not yield dicarbon compounds; and, secondly, of having the silver atom which is not displaceable by potassium standing in union with nitrogen instead of carbon. I have always felt the disconnection of the silver from the nitrogen to be a weak point in my formula, but, as stated in my first paper on the subject (Trans., 1884, 22), the supposed formation of fulminates from nitrous acid and alcohol make this disconnection difficult to allow. This formation having since then been disproved by Mr. Kawakita and myself (*loc. cit.*, 27), the difficulty it caused is removed; and now the study of mercury sulphites further inclines me to assign to the mercury or silver in a fulminate a direct connection with nitrogen, as in the modified formula given above.

Sulphur, Selenium, and Tellurium Sulphoxides are Sulphites.

In this Journal (Trans., 1885, 218, and in earlier papers, in conjunction with Mr. Shimosé), one of us has given to the compounds which sulphuric oxide forms with sulphur, selenium, and tellurium, formulæ like this: $O_2S\overset{O}{\angle\!\!\diagdown}Te{=}Te\overset{O}{\angle\!\!\diagdown}SO_2$, in which the element is represented as having gone half into direct union, half into oxylic union with the sulphuryl. Now, doing this makes them sulphites in constitution, and such they must apparently be taken to be.

They are hydrolysed by water partly into sulphurous acid and what is equivalent to a base:—

$$Se_2(SO_3)_2 + 2H_2O = (Se + SeO_2) + H_2SO_3.$$

They are also partly hydrolysed, like silver sulphite, into metal and sulphuric acid:—

$$Te_2(SO_3)_2 + 2H_2O = 2Te + 2H_2SO_4.$$

They stand in the same relation to the sulphites of strong metals as the corresponding chlorides do to metal chlorides. They resemble salts of the halogens in some of their relations. They are not only formed by the direct union of their quasi-metal with the sulphur trioxide, but can to a certain extent be decomposed again into these by heat in a vacuum; thus, the selenium compound (Trans., 1885, 203), decomposes much as platinous chloride does:—

$$Se_2(SO_3)_2 = 2Se + (SO_3)_2 \qquad Pt_2Cl_4 = 2Pt + 2Cl_2.$$

The selenium compound, like the chlorides of selenium, dissolves in fuming sulphuric acid without decomposition. When thus dissolved, it is decomposed, like a sulphite, by hydrochloric acid:—

$$Se_2(SO_3)_2 + 2ClH = Cl_2Se_2(SO_3) + SO_3H_2,$$

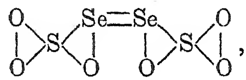
and this compound, not yet isolated (*loc. cit.*, 195), reacts with more hydrochloric acid, just as the corresponding chloride sulphite of mercury (section of this paper on "Mercurosic Sulphite") does with water:—

$$Cl_2Se_2(SO_3) + ClH = Cl_2Se_2 + ClHSO_3$$
$$Cl_2Hg_2(SO_3) + (HO)H = Cl_2Hg_2 + (HO)HSO_3.$$

Admitting these compounds to be sulphites, a further illustration that sulphites resemble haloïd salts is seen in their formation direct from metal and sulphuric oxide:—

$$2Te + (SO_3)_2 = Te_2(SO_3)_2.$$

In a previous paper by one of us, these compounds have been treated as substitution representatives of sulphuric peroxide, SO_4, thus:—



and such they remain when regarded also as sulphites; for just as hypochlorous oxide may be regarded as chlorine hypochlorite, so may sulphuric peroxide (if SO_4 expresses its composition), be regarded as oxygen sulphite, $O\langle^{O}\rangle SO_2$, or the compound $ClHSO_3$ as chlorine hydrogen sulphite, $\left.\begin{matrix}HO\\Cl\end{matrix}\right\}SO_2$, which in reactions it proves to be.

NOTE BY E. DIVERS ON SULPHURIC OXIDE.—In the paper on "The Constitution of some Non-saturated Oxygenous Salts" I was led to discuss the constitution of sulphuric oxide. I pointed out the strong probability there is of this oxide being *sulphuryl sulphate*, and in a more recent paper, in conjunction with Mr. Shimidzu, I gave further experimental evidence in favour of this view. I would now make good an omission in not calling attention to a synthesis of sulphuric oxide, effected many years ago by Odling and Abel (*Chem. Soc. J.*, 7, 2), which leads to the adoption of the same view. Sulphuryl bromide and silver sulphate heated together yield silver bromide and sulphuric oxide:—

$$(SO_2)Cl_2 + Ag_2SO_4 = (SO_2)SO_4 + 2AgCl.$$

In using the name *sulphuryl sulphate*, it is not suggested that there is any difference in the two sulphur-atoms, sulphuryl sulphate being neither more nor less than sulphuryl oxide doubled:—$[O_2S : O_2 : SO_2]$.

The Relation of Selenites to Sulphites.

With the exception of a few unstable compounds, all sulphites have the hemihaloïd or sulphonic constitution. It may be otherwise with

selenites in consequence of the more basylous character, yet, on the whole, much weaker combining power, of selenium; and dioxylic selenites may be the common form.

Ethyl selenite is dioxylic and easily prepared; ethylselenonic acid or ether is unknown. The existence of methylselenonic acid is not certain, for Wöhler and Dean's results are not conclusive on this point.

Metallic selenites are generally considered to have a family resemblance to sulphites; or, perhaps, it would be more correct to say that they are *assumed* to have it. If they really are like sulphites, then they cannot but have the same constitution, but if they are not like sulphites they may differ in constitution and be dioxylic. They do exhibit many unlikenesses to sulphites, but these are hardly such as would suggest that the selenites differ from the sulphites in being dioxylic. Their differences are, rather, such as may be attributed to selenious acid being a more condensed acid than sulphurous acid, and to the feebler affinities of selenium. If, though hemihaloïd, selenites do not oxidise in the air like sulphites, that is only because for oxidation to take place it must proceed simultaneously on the metal and on the chlorous radicle: therefore, because of the selenium, sodium selenite does not oxidise; and because of the silver, silver sulphite does not; whilst sodium sulphite does oxidise because the sodium and sulphur take the oxygen between them. (See, further, the section on the "Oxidation of Sulphites.")

Among the undoubted resemblances of selenites to sulphites, are some of those peculiarities which distinguish sulphites from oxygenous salts generally, and connect them with haloïd salts. Mercury and silver selenites have a degree of insolubility in nitric acid which, though less than that of sulphites, is still far more than sufficient to enable free selenious acid to precipitate them from the nitrates. Mercuric selenite* is soluble in potassium selenite; so is mercuric oxide; and the solutions are not precipitable by potassium hydroxide. Further agreement fails. Mercurous selenite is not decomposed by potassium selenite into mercuric salt and mercury, and silver selenite does not dissolve in potassium selenite. This is somewhat remarkable, but is probably due to the affinities of selenium being so much weaker than those of sulphur and to silver forming less stable compounds than mercury with selenium, as well as with sulphur, silver sulphite being completely decomposed by mercury nitrates. The points of agreement, however, between selenites and sulphites leave but little doubt that the former, like the latter, have a hemihaloïd constitution.

* The insoluble normal selenite. We have not succeeded in preparing Berzelius's soluble acid selenite.

But when silver selenite is treated with ethyl iodide, it yields dioxylic selenious ether, from which metallic selenites would appear also to be dioxylic, as Michaelis and Landmann have suggested they are, instead of being hemihaloïd like metallic sulphites. It cannot be admitted, however, that the iodide test is sufficient by itself to settle the constitution of an oxylic salt, for it gives conflicting testimony as to the constitution of nitrites. Only silver selenite yields the selenious ether; with potassium selenite it is difficult to get a reaction, and when this occurs, it leaves the selenium wholly deoxidised. Since ethylselenonic acid cannot be prepared by the oxidation method, it does seem allowable to suppose that in the reaction of the silver selenite a selenylic group changes into a selenosic one, so as to enter into oxylic union with the ethyl. To suppose this, is a way out of the difficulty certainly much easier than it would be to consider metallic selenites as dioxylic salts.

The Analogue of Sulphurous Acid among Carbon Compounds.

In the discussion of the paper by one of us on the constitution of some non-saturated oxygenous salts, Professor Tilden drew attention to the modification that might be needed in the present view of the constitution of carbonates, if that which was therein advocated for the sulphites should be adopted. The point then raised is a very interesting one, and has suggested to us a further ground for recognising the sulphonic constitution of sulphites, and also for regarding sulphur as only quadrivalent in sulphates as well as in these salts.

Beyond the fact that both sulphites and carbonates are easily decomposable salts, there is nothing specially to connect the two classes of salts. Indeed, even as regards their decomposability, the two classes could not be more unlike than they are in their mercury and silver members. Besides, carbonates are not oxidisable, whilst sulphites are readily oxidisable. It would, therefore, seem strange to require that a similar constitution should be found for the two classes of salts. Rather than this, there is surely a strong presumption that their constitution must be unlike. Nothing is more certain than that carbonates are dioxylic salts; nothing, therefore, would seem more likely than that sulphites should not be dioxylic.

Sulphites find their real analogue among carbon compounds, not in carbonates, but in *formates*, although differing from these in having the double atom of oxygen in their radicle, and in having the hydrogen, which in the acid is joined to the radicle, displaceable by metal.

Both sulphites and formates are monoxylic; both suffer oxidation to salts of dioxylic acids; and both suffer hydrolysis with similar

effects when the basilous radicle is silver or mercury. The oxidisability of formates has always been remarkable, as contrasted with the high degree of stability of the acetates (and higher homologues), in presence of powerful oxidising agents. Now the difference in this respect between formates and acetates is due to the fact that the last remaining hydrogen-atom of methane (aldehydic hydrogen) is readily oxidisable, whilst methyl in place of it is not oxidisable. But this is precisely analogous to what was said in the former paper as to the reason why most metallic sulphites are oxidisable and organic sulphites are not. Methylsulphurous acid and acetic acid—

$$\begin{matrix}Me\\HO\end{matrix}{>}SO_2,\qquad \begin{matrix}Me\\HO\end{matrix}{>}CO,$$

do not oxidise, whereas sulphurous acid and formic acid do oxidise.

$$\begin{matrix}H\\HO\end{matrix}{>}SO_2 + O = (HO)_2SO_2,\qquad \begin{matrix}H\\HO\end{matrix}{>}CO + O = (HO)_2CO.$$

In this oxidation, the carbon does not change in valency; therefore, there is no reason to consider the sulphur as doing so. There is good evidence of sulphur being quadrivalent in sulphites, and therefore also in sulphates. If the sulphur is quadrivalent, the oxygen of sulphuryl forms a bivalent double atom; and that it does so is rendered still more probable by its apparent solidarity in the changes which the sulphuryl may undergo,* and by sulphuryl functioning so very like carbonyl.

The hydrolysis of silver sulphite affects, of course, the whole salt, because its acid is bibasic though monoxylic, whilst the hydrolysis of silver formate affects only half the salt; in both cases, metal is replaced by the hydrogen of the water:—

$$\begin{matrix}AgO\\Hg\end{matrix}{>}SO_2 + OH_2 = 2Ag + (HO)_2SO_2$$

$$2\begin{matrix}AgO\\H\end{matrix}{>}CO + OH_2 = 2Ag + (HO)_2CO + \begin{matrix}HO\\H\end{matrix}{>}CO.$$

Sulphurous acid and formic acid both readily convert mercuric chloride to mercurous chloride. Sodium sulphite and sodium formate are both producible by the action of sodium hydroxide on the respective acid oxides—SO_2 and CO.

Formic acid being the analogue of sulphurous acid, carbonic acid represents sulphuric acid; carboxylic acids sulphonic acids (a relation which has long been recognised); and oxalic acid, hyposulphuric

* If thionyl chloride and silver nitrate do really produce in the first instance nitrosyl chlorosulphonate, as, according to Thorpe, they appear to do (Trans., 1882, 297), an exception after all exists to the statement that oxidation to sulphuryl does not occur in two stages (see Trans., 1885, 215).

acid. Hyposulphuric acid by hydrolysis becomes sulphurous and sulphuric acids; oxalic acid by the same kind of change becomes formic and carbonic acids. The analogy is complete, and surely it must be the case, therefore, that sulphites are only monoxylic salts.

Action of Phosphorus Oxychloride on Sulphites.

In a note to the paper on this subject (Trans., 1885, 207) one of us expressed a doubt as to whether Carius had ever tried, as he was said to have done, the action of phosphorus oxychloride on sulphites. This was done because the results of our own experiments differed apparently from those given on his authority, and because the reference in *Watts's Dictionary* to his paper was found to be wrong. In consequence of the expression of this doubt, Professor Schorlemmer, at a subsequent meeting of the Society, gave the correct reference to Carius's memoir, *Annalen*, **106**, 330, and also some account of what Carius had observed. The back volumes of the *Annalen* have since fortunately come within our reach,* and we have now seen Carius's own words.

The first point important to notice is that he calls attention to the difficulty of getting any sulphite quite dry without decomposition; he succeeded only with the calcium salt, and even that had to be kept in a current of dry air for a long time at 150°. This confirms the surmise contained in the former paper that, in our experiments the sulphites, well-dried as they were supposed to be, must have retained some moisture; only slight action was observed, even when the phosphorus oxychloride was repeatedly distilled off from the sulphite and run back upon it. It was therefore stated that "it is probable that thoroughly dry and pure sulphites are not acted on at all by pure phosphorus oxychloride;" this is just the result of Carius's more accurate experiments. Calcium sulphite is not acted on at all by phosphorus oxychloride at common temperatures, nor even, except to a very slight extent, when the temperature is maintained for some time at 120° under pressure; but it is acted on freely at 150°.

The nature of this action is the second important point in connection with the constitution of sulphites. To make thionyl chloride—for that was his purpose, and not the investigation of the constitution of sulphites—Carius first took 2 mols. of phosphorus oxychloride to 3 mols. of calcium sulphite, in accordance with the equation—

$$3CaSO_3 + 2POCl_3 = Ca_3(PO_4)_2 + 3SOCl_2.$$

Proceeding in this way he failed, not however for want of a reaction at 150°, but because he got large quantities of sulphur dioxide (which

* A set has lately been added to the library of the Imperial University of Japan.

burst his sealed tubes). An equation such as was used in the former paper might serve to express this generation of sulphur dioxide:—

$$6CaSO_3 + 2POCl_3 = Ca_3(PO_4)_2 + 3CaCl_2 + 6SO_2,$$

and, so far, nothing is seen to support the view that sulphites are thionyl compounds—dioxylic salts. As a test of their chemical constitution the reaction has clearly failed, if it does not, indeed, favour their having a sulphonic constitution.

But *some* thionyl chloride is also formed, which makes the matter much less simple; and, besides, half only of the phosphorus oxychloride taken is accounted for in the equation just set down. How material the rest of the oxychloride is to the production of the thionyl chloride, appears from the effects of using a greater proportion of oxychloride in the experiment. Carius found, after repeated trials, that by raising the proportion of oxychloride until equal molecular proportions of the two substances were present, the proportion of thionyl chloride greatly increased, and that of sulphur dioxide became very small. Calcium sulphite can thus be made to yield most of its sulphur as thionyl chloride, but only by using excess of phosphorus oxychloride, since without this excess sulphur dioxide is the main product. Now, this sulphur dioxide must be derived from thionyl chloride should phosphorus oxychloride really act on calcium sulphite, and then form thionyl chloride by this action.

For this, however, to be the true explanation of the production of the sulphur dioxide, some of the sulphite and the oxychloride should remain without acting on each other; because in one case the presence of the phosphorus oxychloride must be supposed to preserve in some way the thionyl chloride from conversion into sulphur dioxide, or in the other case some calcium sulphite must react with the thionyl chloride so as to generate sulphur dioxide:—

$$CaSO_3 + SOCl_2 = CaCl_2 + 2SO_2.$$

This is by no means an impossible reaction, but it is as yet unknown to occur, while its doing so here would depend, as above stated, on the improbable condition that the calcium sulphite to take part in it is to be had as wanted even in presence of phosphorus oxychloride, which for some reason has become inactive on it. This, indeed, seems to remove all chance of its being what actually happens; for just in the case where the phosphorus oxychloride is used in abundance, there is thionyl chloride got in abundance, and nearly without sulphur dioxide. The other view of the matter, that phosphorus oxychloride may in some way preserve the thionyl chloride from decomposition, does not need examining. If this is agreed to, then there is nothing to be said for the view that thionyl chloride is the source of the sulphur dioxide.

Taking into account these three points concerning the production of thionyl chloride from a sulphite—that a high temperature is necessary; that an excess of phosphorus oxychloride must be present; and that sulphur dioxide is the principal and primary product when no more than the normal quantity of the reagent is used—it cannot be allowed that the thionyl chloride is the direct product of a reaction between the sulphite and the oxychloride. It is not difficult to find another origin for it.

Gustavson has shown that when phosphorus oxychloride is heated at the temperature Carius employed, 150°, along with boron oxide, not only is some of the boron oxide converted into chloride, but phosphorus pentoxide is produced and unites with unchanged boron oxide. What takes place when it is heated at 150° with calcium sulphite appears, then, to be this: in its own form it remains without action on the sulphite; it behaves potentially as, or else it gradually dissociates into, phosphorus pentoxide and pentachloride; the pentoxide takes calcium oxide from the sulphite, thus setting free sulphur dioxide; and this with the phosphorus pentachloride gives thionyl chloride and phosphorus oxychloride again (Schiff's reaction). The following equations serve to express these reactions:—

$$10POCl_3 = 2P_2O_5 + 6PCl_5,$$
$$6CaSO_3 + 2P_2O_5 = 2Ca_3(PO_4)_2 + 6SO_2,$$
$$6SO_2 + 6PCl_5 = 6SOCl_2 + 6POCl_3.$$

Three-fifths of the phosphorus oxychloride begun with are thus regained. In practice, Carius found an extra half of the oxychloride to be excess enough to use, which is quite intelligible, since the excess can serve over and over again. The large quantity of sulphur dioxide which forms when these proportions are greatly altered in favour of the calcium sulphite, is to be traced to the action of the phosphorus pentachloride upon the excess of calcium sulphite instead of upon the sulphur dioxide, as is shown by the following equation, intended to take the place of the last one in the scheme of reactions just formulated, on the supposition that 15 mols. of calcium sulphite are present in addition to the 6 mols. there set down:—

$$15CaSO_3 + 6PCl_5 = 3Ca_3(PO_4)_2 + 6CaCl_2 + 9SOCl_2 + 6SO_2.$$

With the other $6SO_2$ liberated, but now not decomposed, there are thus obtained $12SO_2$ to $9SOCl_2$. The calcium chloride here shown is a necessary complement to the sulphur dioxide, whatever version of the change be adopted.

In spite, then, of the production of thionyl chloride when sulphites are strongly heated with phosphorus oxychloride, it still remains true that the changes observed *afford no support* to the view that those salts are dioxylic and decomposable according to the equation—

$$3CaSO_3 + 2POCl_3 = (CaO_2)_3(PO)_2 + 3SOCl_2.$$

LVI.—*On the Electrolysis of Aqueous Solutions of Sulphuric Acid, with special Reference to the Forms of Oxygen obtained.*

By HERBERT McLEOD.

DURING the discussion on Electrolysis at the meeting of the British Association at Aberdeen last year, Dr. Lodge remarked that it was well known that when Wollaston wires are used as electrodes in the decomposition of acidulated water, a considerable quantity of the oxygen is liberated in the form of ozone.

The following papers contain references to the production of ozone by this process:—

Shönbein (1840), *Ann. Phys. Chem.*, **50**, 616—635. "Beobachtungen über den bei der electrolysation des Wassers und dem Ausströmen der gewöhnlichen Electricität aus Spitzen sich entwickelnden Geruch." Five or six times diluted sulphuric acid [from 23·5 to 26·9 per cent. by weight] is best. Phosphoric acid and other solutions when electrolysed produce the same odour.

De Marignac (1845), *Compt. rend.*, **20**, 808—811. "Sur la production et la nature de l'ozone." The liquid used was water charged with sulphuric acid and kept cool. The size of the electrode, the strength of the solution, and the quantity of ozone produced are not stated.

Williamson (1845), *Mem. Chem. Soc.*, **2**, 395—398. "Some Experiments on Ozone." Liquid used consisted of 1 volume of sulphuric acid and 3 of water [38 per cent.]. No measurements of the quantity of ozone are given, as the experiments were made on the assumption that ozone was a peroxide of hydrogen.

H. Meidinger (1853), *Annalen*, **88**, 57—81. "Ueber voltametrische Messungen." The acid used had a density of 1·3. Small quantities of ozone were produced and large quantities of "peroxide of hydrogen."

Baumert (1853), *Ann. Phys. Chem.* **89**, 38—55, and *Phil. Mag.* [4], **6**, 51—63. "Ueber eine neue Oxydationsstufe des Wasserstoffs und ihr Verhältniss zum Ozon." Electrolytic oxygen obtained by electrolysis of dilute sulphuric acid with large positive plate and small negative electrode passed through solution of potassic iodide and afterwards through sulphuric acid, and the gain of weight of the absorption apparatus determined. In one experiment, an increase of 0·0133 in six days was obtained, and in another 0·0149 in eight days.

H. Meidinger (1854), *Chem. Soc. J.*, **7**, 251—255. "On the occurrence of Ozone and Peroxide of Hydrogen in the Electrolysis of Sulphuric Acid." The positive electrode used was 20 mm. long and

$\frac{1}{2}$ mm. thick. The acid seems to have had a density of 1·4. 253 c.c. of hydrogen and 40 c.c. of oxygen were evolved in 19 minutes. When the oxygen was heated, no change of volume could be perceived, and when the gas was acted on by solution of potassic iodide there was a diminution of volume equal to $\frac{1}{300}$th. The acid that had been electrolysed decomposed potassic iodide and so was supposed to contain peroxide of hydrogen, but no determination of its quantity was made. He thinks that if the temperature were sufficiently lowered, pure ozone might be produced. The best acid to give hydrogen and oxygen in proper proportions has a density of 1·1, the negative electrode should be a wire and the positive a plate of not too small dimensions.

Andrews (1855), *Phil. Trans.*, 1856, 1—14. "On the Constitution and Properties of Ozone." The acid used was made by mixing 1 volume of sulphuric acid with 7 of water [20·81 per cent.]. The positive electrode was a bunch of fine wires, and the negative electrode a platinum plate; the liquid was cooled by ice and water. The electrolytic oxygen was passed through a solution of potassic iodide acidified with hydrochloric acid, at the rate of about 750 c.c. of gas per hour. The acid solution was found to give the same results as a neutral solution [a statement contested subsequently by Brodie]. After passing through the potassic iodide, the gas was conducted through drying tubes and the increase of weight determined. The quantity of iodine liberated was also determined volumetrically. Mean of five experiments gave 0·0041 gram of ozone for 1 litre of gas. If ozone is O_3, this number must be multiplied by 3, giving 0·0123 gram or 0·85 per cent. [He says, "Pure water does not absorb ozone."]

Tyndall (1862), *Phil. Trans.*, 1862, 84—86. In his second memoir—"On the Absorption and Radiaton of Heat by Gaseous Matter," used electrolytic oxygen. Small electrodes, less than one square inch in area, were employed, but the exact size is not stated. The quantity of ozone was not determined, but he says, "The quantities of ozone with which I have operated must be perfectly unmeasurable by ordinary means."

L. Soret (1863), *Arch. des Sciences*, **16**, 208—215; *Compt. rend.*, **56**, 390—393. "Sur la production de l'ozone par l'électrolyse et sur la nature de ce corps." The electrodes were very fine wires of platinum-iridium; when platinum is used, a black deposit is formed on the wires which destroys some of the ozone. The acid used contained 1 volume of sulphuric acid to 5 of water [26·9 per cent.]. At a temperature of 5° or 6°, oxygen containing 1 per cent. of ozone was produced (on the assumption that to one equivalent of iodine liberated from the potassic iodide corresponds one equivalent of ozone considered

as an allotropic modification of oxygen). When the acid was cooled with ice and salt, 2 per cent. was formed. [As with Andrews' results, these numbers must be multiplied by 3, so that 3 and 6 per cent. were really obtained.]

Brodie (1864), *Chem. Soc. J.*, **17**, 293. In a paragraph at the end of his paper "On the Organic Peroxides theoretically considered," states that peroxide of hydrogen is not formed during electrolysis, and he thinks that the peroxide of sulphuric acid, H_2SO_5, is present.

C. Hoffmann (1867), *Ann. Phys. Chem.*, **132**, 607—618. "Einige Versuche über die bei der Elektrolyse des Wassers auftretenden Mengen von Ozon und Antozon." A negative wire used and a positive plate, but the dimensions are not given. Gases were not collected, but the relative oxidising action of the gas and the liquid was determined.

Berthelot (1878), *Compt. rend.*, **86**, 71—76, and *Ann. Chim. Phys.* [5], **14**, 354—361. Acid of density 1·4 was used; the positive electrode was of fine platinum wire, sealed into a glass tube. The size of the wire is not given. 910 c.c. = 1·250 grams of oxygen were collected and contained 6·6 mgrms. of ozone [0·528 per cent.]. Active oxygen in the liquid (not hydroxyl) was 44 mgrms. This Berthelot supposes to be present as persulphuric acid. The liquid effervesced. Phosphoric acid gave ozone, but no oxidising liquid. When sulphuric acid, H_2SO_4,H_2O, was used, a small quantity of peroxide of hydrogen was formed containing a quantity of active oxygen, only $\frac{1}{10}$th of that present as persulphuric acid. With the acid, $H_2SO_4,\frac{1}{2}H_2O$, only half this quantity of peroxide of hydrogen was produced.

Schöne (1873), *Ber.*, **6**, 1224—1229. "Ueber das Verhalten von Ozon und Wasser zu einander." The percentage of ozone by volume in the electrolytic oxygen varied between 3·29 and 8·63.

Carius (1874), *Annalen*, **174**, 1—30. "Verhalten das Ozons gegen Wasser und Stickstoff." The acid used was made by mixing 1 "part" of sulphuric acid with 5 of water, and the positive electrode consisted of a very thin platinum-iridium wire 15 mm. long. 100 c.c. of the oxygen contained quantities of ozone varying between 1·438 and 3·44 c.c.

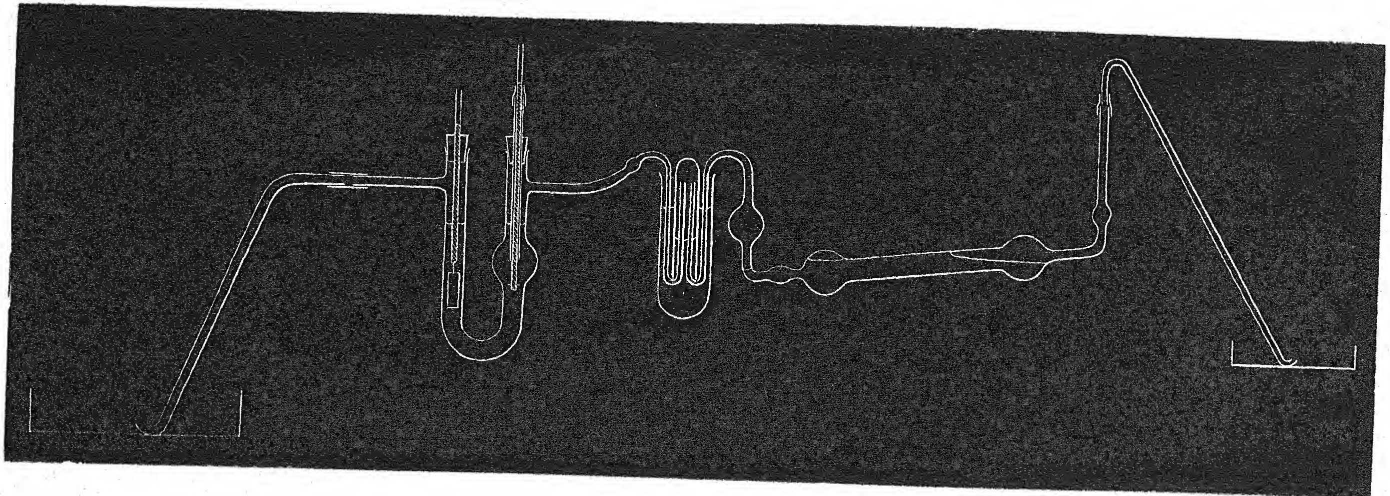
Many of the papers just cited were consulted after the completion of the experiments described in this paper, and it will be seen that some of the results obtained have been anticipated by other experimenters.

As it appeared to be of interest to determine what quantity of ozone is generated during the electrolysis, a series of experiments was instituted in the hopes of throwing some light on the phenomena of the electrolysis of dilute sulphuric acid under various conditions.

In the preliminary experiments, the hydrogen which was evolved from a pole of platinum foil was collected and measured, and the gas from the positive pole, which was of fine wire, was passed through a solution of potassic iodide mixed with hydrochloric acid. The quantity of ozone was calculated on the assumption that only hydrogen, oxygen, and ozone were produced during the electrolysis. Subsequently the oxygen was also collected, when it was at once seen that there was a great deficiency of oxygen, and on adding potassic iodide to the acid which had been electrolysed a considerable quantity of iodine was liberated. This was at the time supposed to be hydroxyl, and means were adopted to prevent its being carried by the oxygen into the potassic iodide used for absorbing the ozone. For this purpose a tube containing potassic dichromate was interpolated, but after it had been in use for some time it was noticed that the dichromate was entirely unaffected, and on testing the acid with potassic dichromate and ether it was found that the oxidising substance is not hydroxyl. Shortly after this observation, Mr. Madan called my attention to a paper by Brodie, on "Organic Peroxides theoretically considered" (*Chem. Soc. J.* (1864), **17**, 281—294), at the end of which is the statement that, during the electrolysis of dilute sulphuric acid, an oxidising substance is produced which does not give the reactions of peroxide of hydrogen, but which may be the hydrate of SO_4, or H_2SO_5. In all probability, the compound is Berthelot's persulphuric acid, the anhydride of which he obtained by the action of the electric effleuve on a mixture of sulphurous anhydride and oxygen. I have not yet examined this compound, but I may mention that during a visit to my laboratory, Mr. C. E. Groves found that after boiling the liquid, it produced perchromic acid when shaken with potassic dichromate and ether.

In the early experiments, an error was probably introduced in the determination of the quantity of ozone by the employment of an acid solution of potassic iodide. Brodie showed that a strong solution of hydriodic acid gives results much too high, and although my solution was dilute and, in fact, almost of the strength that Brodie found to give nearly correct results, yet it will be safer to reject all the numbers, although it involves the sacrifice of 27 experiments.

The apparatus with which all the recent experiments have been made is the following:—A U-tube (see Fig., p. 595), 16 mm. in diameter, has a bulb blown on one limb, and joined near the top of each limb is a tube to conduct away the gases. The ends of the U-tube are closed with corks. The positive electrode consists of a tube closed at the lower end into which the fine platinum wires are sealed; this tube is filled with mercury to make the electric contact, and it is necessary to boil the mercury in the tube to ensure contact with the fine wires.



APPARATUS USED FOR THE ELECTROLYSIS OF SOLUTIONS OF SULPHURIC ACID. $\frac{1}{6}$ REAL SIZE.

This electrode passes through a slightly wider tube fitted to a cork well soaked in melted paraffin and fixed to the limb of the U-tube on which the bulb is blown, the fine wires being about the level of the bottom of the bulb. The negative electrode consists of a platinum plate welded to a platinum wire which is also fused into a glass tube containing mercury and fitted by a cork to the other limb of the U-tube. The hydrogen passes through the tubulure to a delivery-tube dipping into a pneumatic trough, and is collected in a graduated cylinder. During the electrolysis, the U-tube is placed in a beaker containing a mixture of ice and water which is kept stirred by blowing air bubbles into it through a thistle funnel as suggested many years ago by Harcourt and Esson; the air is supplied from a water-pump, and by this device the apparatus may be left with very little attention. The object of the bulb on the U-tube is to cause the cold convection currents to impinge on the positive electrode and prevent its rising in temperature. The ozonised oxygen passes through a narrow U-shaped tube to the absorption-tube containing solution of potassic iodide, this latter tube being also provided with a narrow U-tube; the free limbs of the U-tubes are covered by a closed piece of glass tube, and the whole stands in a wide test-tube containing water, thus forming a water joint which has been found more convenient than the paraffin joint used by Brodie. The absorption-tube is made of a piece of wide tube with a bulb at each end; it is placed in a slightly inclined position, and is similar to some of those employed in Brodie's experiments. To the further end of the absorption tube, a delivery-tube passing to a pneumatic trough is fixed by a caoutchouc joint, and the oxygen is collected in a 100 c.c. measure. The troughs are shallow tin vessels filled to the brim and of such a depth that the pressure is equal on the liquid in both limbs of the U-tube; as the water is displaced from the graduated measure it flows over the edges of the troughs and thus the pressure remains constant during the whole experiment. The absorption-tube contains about 30 c.c. of a solution of potassic iodide containing 0·75 gram of the salt.

When about 100 c.c. of oxygen have been collected, the electric contact is broken immediately after a bubble has passed through the absorption-tube, the delivery-tubes are removed from the troughs and a tube from an aspirator is connected to the oxygen delivery-tube. The test-tube of the water joint is lowered, the negative electrode removed and the greater part of the acid in the U-tube is withdrawn by means of a pipette. This liquid is saturated with ozone and usually effervesces. A slow stream of air is now drawn through the apparatus for about half-an-hour, so that all the ozone may be deposited in the potassic iodide solution. The apparatus is then dis-

mounted, the remaining acid poured from the U-tube and measured. The contents of the absorption-tube are washed into a flask and mixed with about one-fourth of its volume of dilute hydrochloric acid, when the brown colour of the liquid is much intensified. It is next decolorised by decinormal solution of sodic thiosulphate: the addition of starch is unnecessary, as the disappearance of the brown colour is quite sharply defined. The gases are measured by placing the cylinders in water so that the levels are equalised, the temperature and barometer being simultaneously read. To determine the quantity of oxygen which has formed the oxidising material produced in the acid, 10 c.c. of the liquid are placed in a flask, mixed with water and solution of potassic iodide, and kept in the dark until the following day, as the oxidising action is incomplete until after the lapse of some hours; it is then decolorised by decinormal solution of sodic thiosulphate. The oxidising substance not being identified, the quantities obtained are called "active oxygen," a name used by Berthelot.

The currents used for the electrolysis are measured by a tangent galvanometer, the values of the deflections of which are known. Latterly the wires of the positive electrode have been measured by a microscope micrometer before and after each experiment; and from the mean of the measurements, the area of the electrode is calculated, this combined with the current measured by the galvanometer gives the current density, that is, the intensity of the current at the surface of the positive electrode.

The solutions of sulphuric acid were made by diluting with distilled water some pure redistilled sulphuric acid supplied by Messrs. Hopkin and Williams. Their densities were taken by hydrometers at 15° C., and the quantities of acid they contained were determined by a standard solution of sodic hydrate. The following solutions were used:—

Density.	Percentage of SO_2Ho_2.	Molecules of OH_2 to 1 of SO_2Ho_2.	Density.	Percentage of SO_2Ho_2.	Molecules of OH_2 to 1 of SO_2Ho_2.
1·025	3·92	133·4	1·35	46·459	6·3
1·05	7·373	68·4	1·4	51·333	5·2
1·075	11·122	43·5	1·45	55·421	4·38
1·1	14·611	31·8	1·5	60·978	3·48
1·15	21·061	20·4	1·55	65·755	2·83
1·2	27·533	14·3	1·6	69·825	2·35
1·25	34·272	10·4	1·65	74·440	1·87
1·3	40·105	8·1	1·7	78·592	1·48

Various forms of electrode have been tried. In some of the preliminary experiments, pieces of Wollaston wire about 0·03 mm. in

diameter were used. In others, some drawn wires about 0·045 mm. in diameter and flattened, were fused into the glass. One electrode was made with six wires, 0·047 mm. in diameter, the total length of the wires being 104 mm. A series of experiments was made with this electrode, the wires being shortened after each electrolysis, until the total length was only 6 mm. As the wires were shortened the quantity of ozone produced increased, the current being approximately the same in all cases, so that it appears that the formation of ozone depends on current density.

In the first set of experiments of which the results are given below, an electrode was used consisting of six wires, each about 1 mm. long and 0·045 mm. in diameter. Duplicate experiments were made, commencing with acid of density 1·025 and proceeding to that of 1·35. In the last experiment, the current was noticed to be very irregular, which was attributed to a bad contact in the battery, but after cleaning the binding screws there was no improvement, and the experiment was stopped. On examining the electrode it was found that the wires had been much attacked, three of them had almost disappeared, and the remainder were very much thinned. The negative electrode was blackened at its lower edge, which was thought at first to be due to the precipitation of lead from the sulphuric acid, but boiling nitric acid did not remove the stain: on heating the plate red hot, the black colour was at once destroyed and the metal became lustrous, so that the platinum dissolved from the positive electrode had been partially deposited on the negative. It was afterwards noticed that in determining the "active oxygen," in the acid that had been electrolysed, after the brown colour of the iodine had been discharged and before the liquid was quite decolorised, it assumed the pink colour of platinic iodide.

The next electrode was made with platinum wire containing 15 per cent. of iridium, this dissolved in the same manner in the acid of density 1·35.

As the electrodes with fine wires are somewhat troublesome to make, it was hoped that a thicker wire, but of such a length as to expose the same surface and thus maintain the same current density, would be equally efficacious. An electrode was therefore made with a piece of wire, 0·33 mm. in diameter and 0·6 mm. long, but this gave less ozone, although the "active oxygen" was increased.

The next electrode consisted of a fine platinum-iridium wire fed through a capillary tube, so that a fresh piece could be used for each experiment. The resistance of the wire, however, made the operation very slow and the electrode was abandoned.

A new electrode was then made with a single wire 6 mm. long, and placed vertically in the tube. This gave less ozone; but a similar

electrode with the wire horizontal produced a larger quantity. This variation seems to be due to the heat generated in the wire by the current: when the wire is vertical, the evolved gas travels up the wire, and if this is heated some of the ozone will be destroyed; with the horizontal wire, however, the gas at once passes into the cold liquid and the ozone is preserved.

The next electrodes consisted of two wires projecting about 3 mm.; it appeared occasionally that one of the wires made a better contact with the mercury than the other, so afterwards a single wire was passed across the tube and projected about 3 mm. on each side. This form of electrode was used for the remaining acids, a new one being made for each pair of experiments.

Another series of experiments with acids of densities from 1·025 to 1·25, was made with an electrode of one Wollaston wire 0·027 mm. in diameter projecting on each side of the tube, having a total length of 5·3 mm. This was not much attacked by the acid, and I began to think that the previous destruction of the electrodes was due to the presence of a trace of chlorine in the distilled water, but when the acid of density 1·3 was used, the platinum was dissolved, and with the 1·35 acid the electrode had almost disappeared, when 53 c.c. of oxygen had been collected. New electrodes were then made for each experiment, but the series was not continued beyond the acid of density 1·5, as the results were so similar to those obtained with the thicker wires.

As electrolysis seems a convenient process for obtaining ozonised oxygen, it appeared to be worth while to endeavour to construct an apparatus which would yield it more rapidly than the one above described, which has never produced 100 c.c. in less than an hour, and has usually taken very much longer. Two things are essential, a high current density and the electrode being kept cool. The latter condition was fulfilled by blowing a hole on the side of a U-tube, and fusing on to it a small circular electrode made of platinum foil, and surrounding the edge of the platinum disc with arsenic glass or white enamel, which was recommended to me some years ago by Mr. Crookes. The enamel is very fusible, and as it adheres strongly to the platinum and fuses well into the glass, it retains the platinum firmly in its place. When the U-tube is placed in ice and water, the heat produced is rapidly conducted away through the plate of metal. The area of the electrode exposed inside the tube was about 1·9 mm. in diameter, and it was not found possible to obtain a high enough current density with the U-tube employed, for the resistance of the acid would not allow a sufficient quantity of electricity to pass. The result was that the percentage of ozone was only about half that obtained from the same acid with the fine wire electrodes. No doubt

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if a wider U-tube had been employed, the results would have been more favourable.

It may be well to give an example of the observations and calculations made in one experiment which will show all the data from which the results are obtained. I select the one giving the maximum quantity of ozone when the first electrode was used.

Jan. 12, 1886. Electrolysis of acid of density 1·075.

Electrode of six platinum wires 6 mm. long and 0·045 mm. diameter.

Area of electrode at sides $= 0{\cdot}045 \times \pi \times 6 = 0{\cdot}8482$ sq. mm.

" " ends $= 0{\cdot}045^2 \times \frac{\pi}{4} \times 6 = 0{\cdot}00954$ sq. mm.

Total area.................. $= 0{\cdot}85774 =$ 0·0085774 sq. cm.

8 cells of Grove used.

Started	9.45, galvanometer deflection	11°
	9.50 " "	11·2°
	9.54 " "	11·3
	10.0 " "	11·4
	10.40 " "	11·6
Stopped	11.7	

Mean deflection 11·3°; current = 0·4294 ampère.

Duration of experiment = 82 min.

Aspiration started at 11.12; stopped 11.38.

59·7 c.c. of acid in U-tube.

10·5 c.c. of acid mixed with potassic iodide solution.

Decolorised next morning; 7·0 c.c. of decinormal solution of sodic thiosulphate required (1 c.c. of solution = 0·000788 gram of oxygen).

$$7{\cdot}0 \times 0{\cdot}000788 = 0{\cdot}005516. \quad \frac{0{\cdot}005516 \times 59{\cdot}7}{10{\cdot}5} = 0{\cdot}031362 \text{ gram}$$

"active oxygen."

98·1 c.c. of oxygen were collected and measured at 9° C., and bar. 758·3 mm.

261 c.c. of hydrogen were collected and measured at 9°, and bar. 758·3 mm.

$$\begin{array}{r} 758{\cdot}3 \\ 8{\cdot}6 \\ \hline 749{\cdot}7 \end{array} \text{ pressure of aqueous vapour at } 9°.$$

$$\frac{98{\cdot}1 \times 749{\cdot}7}{760 \times (1 + [0{\cdot}003665 \times 9])} = 93{\cdot}68 \text{ c.c. of oxygen at } 0°, \text{ and}$$

760 mm.

$$\frac{261 \times 749 \cdot 7}{760 \times (1 + [0 \cdot 003665 \times 9])} = 249 \cdot 2 \text{ c.c. of hydrogen at } 0°, \text{ and}$$

760 mm.

$0 \cdot 09368 \times 1 \cdot 4336 = 0 \cdot 13430$ gram of oxygen.

$0 \cdot 2492 \times 0 \cdot 0896 = 0 \cdot 022328$ gram of hydrogen.

The liquid from the ozone absorption-tube required 10·05 c.c. of decinormal solution of sodic thiosulphate to decolorise it (1 c.c. = 0·002366 gram ozone).

$$10 \cdot 05 \times 0 \cdot 002366 = 0 \cdot 02378 \text{ gram ozone.}$$

Of the ozone passing into the potassic iodide solution, $\frac{1}{3}$ of the oxygen is fixed, and $\frac{2}{3}$ passes on and is collected with the ordinary oxygen.

$$0 \cdot 02378 \times \frac{2}{3} = 0 \cdot 01585.$$

Total oxygen	=	0·13430 gram.
		0·01585
Ordinary oxygen	=	0·11845 gram.

This ordinary oxygen was mixed with the ozone as it left the electrolysis apparatus.

Oxygen	0·11845
Ozone	0·02378
	0·14223

$$\frac{0 \cdot 02378 \times 100}{0 \cdot 14223} = 16 \cdot 719 \text{ per cent. ozone by weight.}$$

In order to make the results of the different experiments comparable, the various products are reduced to molecules, and compared with 100 molecules of hydrogen which is the only constant.

$\frac{0 \cdot 022328}{2} = 0 \cdot 011164$ molecule of hydrogen.

$\frac{0 \cdot 11845}{16} = 0 \cdot 007402$ atoms of oxygen in the form of ordinary oxygen.

$\frac{0 \cdot 02378}{16} = 0 \cdot 001485$ " " " ozone.

$\frac{0 \cdot 031362}{16} = 0 \cdot 001960$ " " " "active oxygen."

$\frac{0 \cdot 011164}{0 \cdot 011164} \times 100 = 100$ molecules of hydrogen.

$\frac{0 \cdot 007402}{0 \cdot 011164} \times 100 = 66 \cdot 302$ atoms of oxygen in the form of ordinary oxygen.

$$\frac{0{\cdot}001485}{0{\cdot}011164} \times 100 = 13{\cdot}356 \text{ atoms of oxygen in the form of ozone.}$$

$$\frac{0{\cdot}001960}{0{\cdot}011164} \times 100 = 17{\cdot}556 \quad \text{,,} \quad \text{,,} \quad \text{,,} \quad \text{“active oxygen.”}$$

The total number of atoms of oxygen for 100 molecules of hydrogen should obviously be 100.

$$\begin{array}{r} 66{\cdot}302 \\ 13{\cdot}356 \\ 17{\cdot}556 \\ \hline 97{\cdot}214 \end{array}$$

The total is usually a little less than 100 (occasionally a little above), this loss seems due to absorption of oxygen by the water in which it is collected.

The ratio of the gases is obtained by dividing the volume of hydrogen collected by the quantity of oxygen. The volume of the oxygen collected being equal to the volume of ordinary oxygen plus the volume of ozone—if our views of the constitution of ozone are correct.

$$\text{Ratio of gases} = \frac{249{\cdot}2}{93{\cdot}68} = 2{\cdot}660.$$

$$\text{Quantity of hydrogen evolved per minute} = \frac{249{\cdot}2}{82} = 3{\cdot}039 \text{ c.c.}$$

1 ampère evolves 6·9549 c.c. of hydrogen per minute. The current used in the experiment was 0·4294 ampère—

$$0{\cdot}4294 \times 6{\cdot}9549 = 2{\cdot}986 \text{ c.c. of hydrogen per minute.}$$

This number is a little less than that observed, doubtless from the mean deflection taken not being the exact one.

If we had taken 11·5° as the deflection of the galvanometer, the current would have been 0·4372 ampère, and—

$$0{\cdot}4372 \times 6{\cdot}9549 = 3{\cdot}034 \text{ c.c. of hydrogen per minute,}$$

which is almost identical with the measured quantity, but the previous number is sufficiently accurate.

The current density is calculated by dividing the current by the area of the electrode in square centimetres:—

$$\frac{0{\cdot}4294}{0{\cdot}0085774} = 50{\cdot}06 \text{ ampères per square centimetre.}$$

This example will render intelligible the following table of collected results. It has been considered advisable to give the method and numbers in detail, for at present it seems difficult to see what bearing they have on the phenomenon of electrolysis.

Date.		Density of acid.	Molecules of hydrogen.	Atoms of oxygen in the form of Ordinary oxygen.	Ozone.	"Active oxygen."	Sum of oxygen atoms.	Per cent. of ozone in oxygen.	Ratio of gases.	H evolved per min. c.c.	Current. Ampères.	H per min. calculated. c.c.	Density of current. Ampères per sq. cm.
Jan. 12	Electrode of six platinum wires about 1 mm. long and 0·045 mm. diameter......	1·025	100	79·348	12·345	6·130	97·823	13·461	2·283	1·833	0·2639	1·835	30·76
13		1·025	100	77·442	11·955	6·158	95·555	13·389	2·341	1·958	0·2829	1·967	32·98
12		1·05	100	72·864	13·053	11·020	96·937	15·184	2·452	3·085	0·4372	3·041	50·97
13		1·05	100	72·850	12·747	11·072	96·669	14·908	2·458	3·261	0·4883	3·396	56·93
11		1·075	100	66·356	13·266	18·076	97·698	16·668	2·659	2·650	0·3828	2·662	44·63
12		1·075	100	66·302	13·356	17·556	97·214	16·719	2·660	3·039	0·4294	2·986	50·06
13		1·1	100	63·688	12·003	20·794	96·385	15·873	2·728	3·163	0·4568	3·177	53·26
15		1·1	100	67·562	11·649	20·556	99·767	14·699	2·728	4·006	0·5678	3·949	66·2
15		1·15	100	59·920	8·955	25·858	94·733	13·016	3·034	3·143	0·4686	3·259	54·63
15		1·15	100	59·782	8·982	27·798	96·562	13·062	3·040	3·224	0·4647	3·232	54·18
18		1·2	100	60·408	6·279	34·334	101·021	9·421	3·097	3·300	0·4568	3·177	53·26
18		1·2	100	59·384	6·543	33·372	99·299	9·917	3·133	2·956	0·4294	2·986	50·06
18		1·25	100	60·692	6·288	31·486	98·466	9·413	3·081	2·916	0·4100	2·851	47·80
19		1·25	100	61·234	6·498	29·986	97·718	9·594	3·049	2·971	0·4216	2·932	49·15
19		1·3	100	71·562	12·243	14·320	98·125	14·608	2·508	3·273	0·4647	3·232	54·18
19		1·3	100	71·886	12·549	14·450	98·885	14·857	2·492	3·224	0·4529	3·150	52·8
20		1·35	100	76·258	9·393	15·486	101·137	10·965	2·423	2·975	0·4177	2·905	48·7
20		1·35	100	79·830	6·738	13·944	100·512	7·791	2·372	?	?	?	?

Electrode was found to have been dissolved. As the current densities are calculated on the assumption that the wire had a uniform diameter during all the experiments, the latter numbers must be much too low.

Date.		Density of acid.	Molecules of hydrogen.	Atoms of oxygen in the form of Ordinary oxygen.	Ozone.	"Active" oxygen.	Sum of oxygen atoms.	Per cent. of ozone in oxygen.	Ratio of gases.	H evolved per min. c.c.	Current. Ampères.	H per min. calculated. c.c.	Density of current. Ampères per sq. cm.
Jan. 25	New platinum iridium electrode. Six fine wires about 1 mm. long and 0·045 mm. diameter	1·1	100	67·368	10·779	19·522	97·669	13·789	2·682	3·043	0·4333	3·014	50·52
25		1·2	100	59·490	6·372	33·178	99·040	9·681	3·137	3·028	0·4255	2·959	49·61
25		1·3	100	70·342	12·345	14·682	97·369	14·944	2·545	3·045	0·4333	3·014	57·46
26		1·35	100	73·858	8·247	16·098	98·203	10·038	2·525	3·110	0·4490	3·123	59·55
26		1·35	100	74·390	7·821	16·038	98·249	9·519	2·513	3·025	0·4490?	3·123?	238·2?
27	Electrode of short thick wire 0·6 mm. long; 0·33 mm. diameter	1·35	100	63·378	2·649	31·822	97·849	4·026	3·070	3·005	0·4255	2·959	60·14
27		1·35	100	64·952	5·076	26·878	96·906	7·204	2·906	2·049	0·2928	2·036	43·47
29	Electrode of platinum iridium wire 6 mm. long. Fed through capillary tube	1·35	100	71·650	9·342	18·436	99·428	11·549	2·567	1·675	0·2411	1·677	32·83
*30		1·35	100	70·580	10·131	17·506	98·217	12·586	2·586	1·607	0·2259	1·571	30·7
30	New electrode platinum iridium wire 6 mm. long. 0·045 mm. diameter. Vertical	1·35	100	69·026	6·870	22·398	98·294	9·078	2·717	3·523	0·5001	3·478	66·32
Feb. 1		1·35	100	69·182	7·917	20·946	98·045	10·277	2·685	2·832	0·3906	2·717	67·49
1	New electrode like last, but wire horizontal..........	1·35	100	—	9·933	18·176	—	—	—	2·802	0·3867	2·689	51·9
1		1·35	100	71·586	9·282	18·820	99·688	11·494	2·571	2·747	0·3983	2·770	68·82
2	New electrode like last	1·35	100	71·076	10·983	17·374	99·433	13·394	2·570	2·606	0·3751	2·609	49·75
6	Electrode with two wires, each about 3 mm. long	1·35	100	70·490	10·932	15·668	97·080	13·423	2·572	3·079	0·4216	2·932	51·76
8		1·35	100	72·682	10·392	16·136	99·210	12·527	2·512	3·012	0·4372	3·041	60·84
9	Similar electrode	1·4	100	73·234	7·995	18·080	99·307	9·841	2·545	3·281	0·4725	3·286	60·65
9		1·4	100	74·992	5·214	18·706	98·912	6·527	2·547	2·202	0·3289	2·287	69·8

* Fresh end of wire.

Date.		Density of acid.	Molecules of hydrogen.	Atoms of oxygen in the form of: Ordinary oxygen.	Ozone.	"Active oxygen."	Sum of oxygen atoms.	Per cent. of ozone in oxygen.	Ratio of gases.	H evolved per min. c.c.	Current. Ampères.	H per min. calculated. c.c.	Density of current. Ampères per sq. cm.
Feb. 10	Electrode with one wire projecting about 3 mm. on each side.	1·4	100	74·380	7·233	17·808	99·421	8·858	2·525	3·458	0·5239	3·644	75·66
10	Similar electrode	1·45	100	71·024	1·164	29·218	101·406	1·616	2·785	2·927	0·4372	3·041	52·81
12		1·45	100	75·286	1·116	24·182	100·584	1·463	2·630	2·334	0·3481	2·421	47·66
12	Similar electrode	1·5	100	76·438	0·717	24·280	101·435	0·930	2·600	1·779	0·2639	1·835	34·43
15		1·5	100	76·224	0·765	22·218	99·207	0·996	2·606	2·489	0·3020	2·100	42·02
15	Similar electrode	1·55	100	78·374	0·648	20·430	99·452	0·821	2·538	1·868	0·2677	1·862	34·57
16		1·55	100	75·736	0·558	23·264	99·558	0·734	2·627	1·877	0·2677	1·862	41·98
16	Similar electrode	1·6	100	79·144	0·543	19·192	98·879	0·681	2·515	1·286	0·1767	1·229	25·57
19		1·6	100	79·264	0·516	18·338	98·118	0·646	2·513	1·133	0·1616	1·124	26·72
Mar. 9	Similar electrode	1·65	100	81·076	0·528	18·220	99·824	0·646	2·457	1·035	0·1503	1·045	21·36
10	Same electrode	1·7	100	83·668	0·699	14·612	98·979	0·828	2·378	0·687	0·0938	0·652	14·22
12	Electrode of two Wollaston wires, total length about 5·3 mm., diam. 0·027 mm..	1·025	100	75·406	13·713	6·066	95·185	15·404	2·365	1·472	0·2145	1·492	49·55
16	Same electrode	1·05	100	70·614	14·553	11·246	96·413	17·099	2·489	1·863	0·2715	1·888	66·69
17	Same electrode	1·075	100	68·306	12·489	14·512	95·307	16·573	2·585	2·184	0·3059	2·127	79·87
19	Same electrode	1·1	100	63·472	13·338	20·786	97·596	17·382	2·754	1·673	0·2411	1·677	65·82
April 5	Same electrode	1·1	100	73·572	12·846	17·782	104·200	16·527	2·719	2·201	0·3135	2·180	85·58
6	Same electrode	1·15	100	60·264	9·999	27·196	97·459	14·236	2·988	1·843	0·2677	1·862	76·55
6	Same electrode	1·2	100	57·902	5·961	32·450	97·413	10·948	3·192	1·304	0·2677	1·862	76·55
7	Same electrode	1·25	100	59·226	5·550	36·436	101·212	8·563	3·177	1·795	0·2639	1·835	79·25
May 21	Same electrode	1·3	100	72·862	11·610	14·182	98·654	13·774	2·482	1·928	0·2791	1·941	102·99*

* Electrode much attacked.

Date.		Density of acid.	Molecules of hydrogen.	Atoms of oxygen in the form of: Ordinary oxygen.	Ozone.	"Active" oxygen.	Sum of oxygen atoms.	Per cent. of ozone in oxygen.	Ratio of gases.	H evolved per min. c.c.	Current. Ampères.	H per min. calculated. c.c.	Density of current. Ampères per sq. cm.
May 24	New electrode. Total length, 5·928; diam., 0·020 mm. . .	1·35	100	72·368	10·200	15·588	98·156	12·379	2·528	2·026	0·2982	2·074	153·95*
24	New electrode. Total length, 5·280; diam., 0·020 mm. . .	1·4	100	76·948	6·693	17·344	100·985	8·039	2·457	1·797	0·2906	2·021	146·5
25	New electrode. Total length, 6·582; diam., 0·016 mm. . .	1·45	100	77·332	3·816	18·552	99·700	4·714	2·504	1·605	0·2259	1·571	127·3
25	New electrode. Total length, 5·972; diam., 0·018 mm. . .	1·5	100	82·660	1·905	19·914	104·479	2·252	2·384	1·211	0·1691	1·176	35·7
27	Flat electrode about 1·9 mm. in diameter, fused on side of U-tube	1·1	100	81·446	6·372	10·870	98·688	7·275	2·334	2·994	0·4294	2·986	15·15
June 1		1·15	100	75·476	6·261	16·038	97·775	7·689	2·510	4·998	0·6982	4·856	24·62
8	Electrode with 10 short wires, 0·047 mm. diam. Total length, 6·788. Area, 0·01019 sq. cm.	1·1	100	65·254	11·253	20·340	96·847	14·710	2·748	3·334	0·4765	3·314	46·76

* Electrode dissolved.

Various estimates of the solubility of ozone in water have been made, and one experiment has been carried out to endeavour to determine the coefficient. The result is so very different from some of those previously obtained, that it must be regarded as only preliminary, and other experiments must be made to confirm it.

The tube used for the absorption of the ozone in the above experiments was filled with water and connected to the electrolysis apparatus containing acid of density 1·075, and a current of electricity was then passed through the acid for 232 minutes, during which time 500 c.c. of hydrogen were evolved. From other experiments, the oxygen may be supposed to have contained about 16 per cent. by weight of ozone, or 11·27 per cent. by volume.

The water in the absorption-tube, which was at the temperature of 14° during the experiment, was mixed with potassic iodide and hydrochloric acid, and decolorised by the decinormal sodic thiosulphate. 0·9 c.c. were required equal to 0·002129 gram of ozone. The volume of the water in the tube was 32 c.c., so that 1 c.c. of water contained $\frac{0 \cdot 002129}{32} = 0 \cdot 00006653$ gram of ozone.

1 litre of ozone weighs 2·1504 grams, and

$$\frac{0 \cdot 00006653 \times 1000}{2 \cdot 1504} = 0 \cdot 03093 \text{ c.c. of ozone in 1 c.c. of water.}$$

The pressure of the ozone in the tube, calculated from the volume per cent. of ozone, was $\frac{1}{8 \cdot 875}$ of an atmosphere for $\frac{100}{11 \cdot 27} = 8 \cdot 875$, so that the coefficient of solubility of ozone from this single observation is $0 \cdot 03093 \times 8 \cdot 875 = 0 \cdot 2745$, which is nearly ten times that of ordinary oxygen, 0·02989.

The coefficient obtained by Schöne (*Ber.*, **6**, 1224—1229) was 0·366 at 18·2°. That obtained by Carius (*Annalen*, **174**, 30) was 0·834 at 1°.

When ozone is passed into a solution of potassic iodide, especially an acid solution, a dense white fume is produced. This is generally said to be hydric peroxide, but I had a suspicion that it at least contained iodic acid. An attempt to prove this was, however, a failure, owing to the omission of a precaution which was obvious when it was too late; however, since the paper was communicated to the Society I have had an opportunity of repeating the experiments in a more careful manner.

About 100 c.c. of ozonised oxygen, containing probably about 15 per cent. of ozone, were collected in a small flask. When the flask was filled, a solution of potassic iodide mixed with about one-third of its volume of dilute hydrochloric acid was introduced into the flask and

agitated with the gas. After a minute or two some sodic hydrate solution was introduced into the flask to fix the free iodine (this was the precaution omitted in the previous experiment), and after agitation the flask was fitted with a cork carrying two tubes, and one of these was attached to a glass tube heated in the centre to the softening point. Between the flask and the hot part of the tube were placed a slip of paper coated with starch, and next a piece of paper with potassic iodide and starch. Beyond the hot portion were two similar papers. Air was slowly drawn through the flask into the tube by an aspirator. The first piece of starch-paper was entirely unaffected, the first piece of potassic iodide and starch-paper was rendered very slightly blue, from the presence of either a trace of ozone or of peroxide of hydrogen. The starch-paper beyond the hot part of the tube became intensely blue, from the iodine liberated by the decomposition of the iodic acid, subsequently the second piece of potassic iodide and starch-paper became equally blue from the action of the free iodine on the starch, for of course the high temperature of the glass would have destroyed ozone or hydroxyl if either had been present.

Note on the Action of Oxygen on Hydrochloric Acid under the Influence of Light.—In the foregoing experiments, it was noticed that when concentrated hydrochloric acid was added to potassic iodide, the liberation of a small quantity of iodine took place, whilst no such result followed the addition of dilute acid. The concentrated acid had been standing in the laboratory for some time in a bottle only partly filled.

It struck me that the reaction might be due to the evolution of a small quantity of chlorine from the oxidation of the hydrochloric acid, and it recalled an observation which I had made several times when preparing a lecture experiment to show the decomposition of water by chlorine. This experiment is done annually, usually in the winter months, by filling a flask with chlorine-water, inverting it in chlorine-water, and placing it in the field for several days; sometimes the solution is entirely decolorised, and at other times the colour remains light yellow even after long exposure. During last winter, two experiments were made, one with some chlorine solution that had been in the laboratory for some time, and the other with some freshly prepared chlorine-water. The first was entirely decolorised and the second was not. This seemed to show that when a certain quantity of hydrochloric acid has been formed, the decomposition of the water is arrested, or at least checked; and it seemed probable also that the process would be reversible, and that hydrochloric acid would be decomposed by oxygen.

To put this to the test six **V**-shaped tubes, closed at one end, were filled with the following liquids :—

1. Saturated chlorine-water.
2. Chlorine-water mixed with an equal volume of distilled water.
3. Concentrated hydrochloric acid, density 1·153, saturated with chlorine.
4. Hydrochloric acid, density 1·1, saturated with chlorine.
5. Hydrochloric acid, density 1·03, saturated with chlorine.
6. Concentrated hydrochloric acid with oxygen in the closed limb.

These tubes were exposed to sunlight on May 5, and left in the field until the 18th. The sunshine was very brilliant on the 5th, 6th, and parts of the 7th, 8th, 9th, 10th, 15th, and 18th.

The dilute chlorine-water was soon decolorised, oxygen being evolved; the concentrated solution retained a colour for some days longer. No gas whatever was evolved from the hydrochloric acid solutions that were saturated with chlorine; and almost the whole of the oxygen was absorbed by the concentrated acid.

No free chlorine remained in what had been the chlorine-water, as it gave no coloration with potassic iodide.

When the hydrochloric acid which had absorbed the oxygen was tested in the same way, a brown coloration was produced.

I am not aware that this fact has been published, at any rate it is not generally known.*

LVII.—*On Essential Oils.* Part III. *Their Specific Refractive and Dispersive Energy.*

By Dr. J. H. Gladstone, F.R.S.

My former papers on the essential oils (*Chem. Soc. J.*, **17**, 1, and **25**, 1) date back to 1863 and 1872. Since that time these substances have been made the subject of many investigations by Riban, Beilstein, Alder-Wright, Armstrong, Tilden, Atkinson and Yoshida, Pattison-Muir, Flavitzky, and others; many new facts have been added to our knowledge, and some advance has been made towards determining the rational constitution of these compounds.

* On the day this paper was read (June 17), there appeared in "Nature" the abstract of a communication by M. Leo Backelandt to the *Bull. Acad. Roy. Belgique* [3], 11, 194, on the oxidation of hydrochloric acid under the influence of light, in which it is shown that when concentrated hydrochloric acid is exposed to sunlight in a badly stoppered bottle, it becomes yellow from liberation of chlorine.

Nevertheless, there remain some most important differences of opinion on the subject, and eminent chemists are still discussing whether the formula of oil of turpentine itself should contain one, two, or three pairs of doubly-linked carbon-atoms. In this paper I propose to bring forward such arguments as may fairly be founded on the phenomena of refraction and dispersion, not considering that this is necessarily the key to the position, but feeling sure that in the conflict of opinions such arguments ought to have considerable weight.

Pattison-Muir (Trans., 1880, 688) perceived the value of the argument from the refraction equivalents, but the essential oils to which he applied it were of uncertain purity. More recently Kanonnikoff (*J. Russ. Chem. Soc.*, **15**, 434) has attempted to solve by means of it the constitution of these and many other organic compounds.

Unfortunately very few of those who have worked on these oils have recorded their refractive index, and still fewer their dispersive power; and although the specific gravity is generally given, it has not always been taken at the same temperature as the optical properties, so that the observations are of little value for the present purpose. Thus I have to fall back mainly on my own observations, which are scattered through several papers in the Transactions of this Society (1870, 101, 147; and 1884, 241), and on some fresh observations the details of which are given in the Appendix.

It may be desirable in the first place to point out briefly the kind of evidence which these optical properties afford. The specific refractive energy of a substance is its refractive index minus unity divided by its density. It is calculated by me for the line A of the solar spectrum, and is therefore represented by the formula $\frac{\mu_A - 1}{d}$. The specific dispersive energy is the difference between the specific refractive energies of the two extreme visible lines A and H, *i.e.*, $\frac{\mu_H - 1}{d} - \frac{\mu_A - 1}{d}$, or $\frac{\mu_H - \mu_A}{d}$. The specific refractive energy multiplied by the atomic weight, $P\frac{\mu_A - 1}{d}$, gives the refraction equivalent. Now the refraction equivalent of a compound body is the sum of the refraction equivalents of its components; and in all the saturated carbon-compounds the refraction equivalent of one atom of carbon is found to be 5·0 for the line A, and that of hydrogen 1·3. It was, however, observed long ago in the *Journal of the Chemical Society* (1870, p. 151), that "all the essential oils of the $C_{10}H_{16}$ type that have been examined, more than 30 in number, give refraction equivalents a little above theory; those of the great turpentine-group generally exceed the calculated number (70·8) by amounts

varying from two to three, those of the orange-group by amounts varying from three to four." It was also observed that the oxygen compounds of this group afforded "another illustration of the increased influence on light of carbon which is uncombined with two atoms of hydrogen or one of oxygen." Subsequently Brühl showed that in every compound in which any carbon-atoms are supposed to be "doubly-linked," each such carbon-atom has a refraction equivalent of 6·1, or, which is the same thing, each pair increases the normal equivalent by about 2·2.

It was also an early observation that the increase of refractive power in the essential oils, aromatic compounds, &c., is attended by a corresponding advance in dispersive power. This advance is proportionally much larger than in the case of the refraction. Its extent may likewise be determined by multiplying the specific dispersive energy by the atomic weight $P\frac{\mu_H - \mu_A}{d}$. These "dispersion equivalents" have been little investigated as yet, but the law appears to hold good among analogous compounds that the dispersion equivalent of a compound is the sum of the dispersion equivalents of its constituents.* Among saturated organic compounds I find the dispersion equivalent of CH_2 to be 0·34 (or more exactly, perhaps, 0·342). It is more difficult to assign an exact value to the two elements themselves, but 0·045 for each hydrogen, and 0·25 for carbon may be accepted as a first approximation. Again, just as in the case of refraction, the double-linking of a pair of carbon-atoms increases the dispersion equivalent. This increase is greater in the aromatic than in the allyl compounds, amylene, &c.; in the latter the increase is about 0·5 for each pair of carbon-atoms; in the former it is fully 0·8.

The Hydrocarbons.

It is well known that the natural essential oils are generally a mixture of isomeric hydrocarbons of the molecular formula $C_{10}H_{16}$, or $C_{15}H_{24}$, with C_{10} compounds containing one atom or more of oxygen. These have to be separated by fractional distillation, and it is difficult, if not impossible, to obtain the various substances in a state of purity. It is now generally accepted that the isomeric oils of the formula $C_{10}H_{16}$ fall into two groups—the terpenes and the citrenes, or isoterpenes. These two groups, together with the cedrenes, $C_{15}H_{24}$, differ

* There are two or three considerations which show that this law cannot be as trustworthy in the case of dispersion equivalents as it seems to be in the case of refraction equivalents, but it is exact enough for the purpose of this paper. Some dispersion equivalents were calculated by me 20 years ago: *vide Brit. Assoc. Report*, 1866, Trans. of Sections, p. 37.

in boiling point, specific gravity, and rotatory power, and also in specific refractive and dispersive energy. The difference is strongly marked in the table given in the first part of this communication (*Chem. Soc. J.*, 1863, 1), and the average result of these old observations is given below. The terpenes are taken from nine different specimens, including turpentine, mint, anise, thyme, and wormwood: the citrenes from twelve, including orange, lemon, bergamot, carraway, dill, cascarilla, and elder. The specific dispersive energy has been added:—

	Terpenes.	Citrenes.
Boiling point	160° C.	About 174° C.
Specific gravity at 20° C.	0·8617	0·8466
Refractive index for line A	1·4612	1·4636
Dispersion	0·0258	0·0285
Specific refractive energy	0·5361	0·5476
Specific dispersive energy	0·0299	0·0337

The oils of nutmeg and carraway contained both terpenes and citrenes mixed together, and of course it was scarcely possible to separate them. The same appears to be the case with the oil of sage, according to Pattison-Muir.

The Terpenes.

From the figures in the above table, it is easy to calculate the average refraction and dispersion equivalents of the terpenes in my old observations. $P\frac{\mu_A - 1}{d}$ for $C_{10}H_{16}$ will be 72·91, and $P\frac{\mu_H - \mu_A}{d}$ will be 4·07. If, however, we select the three specimens of left-handed turpentine, which gives perhaps the purest terpene, we obtain 72·95 and 4·01 respectively. A carefully prepared specimen from American pine was recently examined, as well as a terpene from oil of mint, the particulars of both of which will be found in the Appendix. Again, Flavitsky has determined the optical properties of a left-handed terpene from Russian turpentine, and, though he has measured the lines α, β, and γ of hydrogen, it is easy to calculate his results for the solar A, and the difference between H and A.*

* This is given in Kanonnikoff's recent paper (*J. pr. Chem.*, 1885, 497). The Continental observers generally measure the three lines of the hydrogen spectrum H_α, H_β, H_γ; of which α and β are coincident with the solar lines C and F. The dispersion in these observations is $\gamma - \alpha$, which is easily converted into the dispersion $H - A$ according to the ratio of 1 to 1·59. The value for A is obtained from C and F upon the basis of $F - C : C - A :: 100 : 29·8$.

The following are the results :—

Natural terpenes.	Refraction equivalent.	Dispersion equivalent.
Old observations	72·91	4·07
Three from pine	72·95	4·01
From American pine	73·11	3·99
From Russian pine	73·12	3·95
From mint	72·91	4·02

But substances of the composition $C_{10}H_{16}$ have been prepared artificially by the action of certain reagents on the natural terpenes or their compounds. Riban (*Compt. rend.*, **78**, 788, and **79**, 314) has determined the refractive indices of his "terebene" and "terebenthene" for the lines C, *b*, and others, at 16° C., with the following results :—

	Terebene.	Terebenthene.
Boiling point	156°	156·5°
Specific gravity at 20°	0·8600	0·8601
Refractive index (C) at 16°	1·4645	1·4665
Specific refractive energy	0·5383	0·5406
Specific dispersive energy (*b* – C)	0·0083	0·0087

The equivalents calculated from these figures for A and H—A are—

	Ref. eq.	Disp. eq.
"Terebene"	72·8	3·81
"Terebenthene"	73·0	4·00

Barbier gives the refractive index of the $C_{10}H_{16}$ regenerated from his liquid $C_{10}H_{17}Cl$, and that from another chloride, for the line D. Unfortunately he does not mention the temperature, but I assume it to be 12°, which seems probable from his paper. The results are as follows :—

	Specimen I.	Specimen II.
Boiling point	157°	157°
Specific gravity at 12°	0·8812	0·8724
Refractive index, line D	1·4692	1·4704
Specific refractive energy	0·532	0·539

These somewhat doubtful data give respectively 72·4 and 73·3 for the line D.

These four artificial hydrocarbons are evidently identical in their refractive energy as well as in their other physical properties with the natural terpene, though they have lost the power of rotating the plane of polarised light.

Now the refraction equivalent of $C_{10}H_{16}$, taking all the carbon at the normal value in saturated bodies, would be 70·8, and the dispersion equivalent would be about 3·24. If we add to these figures 2·2 and 0·8 respectively, we obtain numbers almost identical with those of experiment—

	Found.	Calculated.
Refraction equivalent	73·0	73·0
Dispersion equivalent	4·0	4·04

being a twofold indication that in the terpenes there is only one pair of carbon-atoms doubly-linked.

This result, improbable as it may at first appear, only corroborates the views of those chemists who, on chemical grounds, have held that a terpene requires the addition of only two atoms of hydrogen, or their equivalent, to saturate it.

Very interesting also is the solid inactive *camphene*, $C_{10}H_{16}$, of which Professor Tilden has kindly furnished me with two different preparations. Two solutions of each of these in alcohol were determined, giving the following results:—

Camphene.	Percentage in solution.	Refraction equivalent.	Dispersion equivalent.
1st preparation	28·78	71·82	3·78
"	33·60	72·17	3·84
2nd preparation.....	29·69	71·87	3·57
"	25·88	71·78	3·47

These four refraction equivalents are as accordant as determinations made from solutions can be expected to be, but they are all lower than the equivalents obtained from the liquid terpenes. The same is true of the dispersion equivalents, especially those of the second preparation. Whatever may be the cause of this, we may at least safely conclude that camphene does not contain more than one pair of doubly-linked carbon-atoms; this agrees with the chemical character of the compound, as pointed out by Tilden, for it combines with only one molecule of hydrochloric acid, and is directly converted by oxidation into camphor, $C_{10}H_{16}O$, which is certainly a saturated compound.

The Citrenes.

From the table on page 612, it will be seen that the specific refractive energy of the citrenes examined 23 years ago was 0·5476, and the specific dispersive energy 0·0337. But it must be observed that some of the hydrocarbons included in the calculation were confessedly difficult to rectify. If the four specimens derived from orange and lemon-peel be alone taken (which are perhaps the purest specimens), the specific refractive energy would be 0·5494, and the specific dispersive energy 0·0331; while a carefully prepared specimen of hesperidine from Dr. Wright, more recently examined, gave a specific refractive energy of 0·5513, and a specific dispersive energy of 0·0327. Flavitsky also has determined the optical properties of the hydrocarbon from oil of lemons, giving the specific refractive energy of 0·5579 for Hα, and the specific dispersive energy of 0·0215 for the hydrogen lines α and γ. These figures, reduced as before, give the following values:—

Natural citrenes.	Refraction equivalent.	Dispersion equivalent.
Old observations	74·47	4·58
Four from orange and lemon...	74·72	4·50
Wright's....................	74·98	4·45
Flavitsky's	75·34	4·55

A citrene also, equally with a terpene, is capable of reproduction from its compounds. Riban prepared a substance which he termed isoterebenthene, having the boiling point 175°, a sp. gr. of 0·838 at 25°, a refractive index of 1·4677, and a much higher dispersion than his terebenthene. This gives a specific refractive energy of 0·5581 for the line C, and a specific dispersive energy of 0·0099 between C and *b*.

These figures reduced to the probable values for A, and H—A will give—

	Ref. eq.	Disp. eq.
Artificial citrene	75·1	4·58

Now the increase in both these optical equivalents requires us to suppose that not one, but two pairs of the carbon-atoms in the citrenes are doubly-linked. The figures are as follows:—

Citrenes.	Found.	Calculated.
Refraction equivalent	75·03	75·2
Dispersion equivalent	4·55	4·84

The coincidence of the calculated numbers with the results of experiment is not so close as in the case of the terpenes, but it leaves little room for doubt.

The hydrochlorides of the citrenes seem always to contain 2 mols. HCl, which, with other considerations, has generally led chemists to come to the same conclusion as to their constitution as that deduced above.

Allied to the citrenes are several hydrocarbons produced from essential oils, but having a different amount of hydrogen. If $C_{10}H_{16}$ has two pairs of carbon-atoms doubly-linked, $C_{10}H_{18}$ ought to have only one, and $C_{10}H_{20}$ ought to be a saturated hydrocarbon, while on the other hand $C_{10}H_{14}$ ought to have three. All this is actually the case.

$C_{10}H_{20}$ is a hydrocarbon, which, according to Armstrong and Tilden, frequently occurs among the products of decomposition of the essential oils (Trans., 1879, 745), and which Armstrong considers to be a saturated body, and now designates "cymhydrene."

$C_{10}H_{18}$ is the menthene derived by Atkinson and Yoshida (Trans., 1882, 49) from oil of peppermint.

$C_{10}H_{14}$ is cymene, which is easily prepared from the essential oils by chemical reactions (Wright, *Chem. Soc. J.*, 187, 6863), and probably pre-exists in some of them. It is a well-known member of the aromatic group of hydrocarbons. The figures given below are the mean of 16 different preparations of Wright, described in *British Association Reports*, 1873, 217, and 1874, 20.

That these form a true series is evident from the following table :—

Substance.	Boiling point.	Temp. C.	Specific gravity.	Refractive index.	Specific refraction.	Specific dispersion.
$C_{10}H_{20}$	170° ?	12°	0·8046	1·4369	0·5430	0·0246
$C_{10}H_{18}$	167·4	8·5	0·8137	1·4460*	0·5481	0·0313
$C_{10}H_{16}$	174	—	0·8483	1·4677	0·5513	0·0334
$C_{10}H_{14}$	178	15	0·8605	1·4818	0·5601	0·0406

The refraction and dispersion equivalents of these for A and H is given below, together with the theoretical values calculated on the supposition that the four substances are of the constitution indicated above.

* Reduced from C to A.

Substance.	Refraction equivalent.		Dispersion equivalent.	
	Observed.	Calculated.	Observed.	Calculated.
$C_{10}H_{20}$	76·02*	76·0	3·44	3·4
$C_{10}H_{18}$	75·64	75·6	4·32	4·1
$C_{10}H_{16}$	75·03	75·2	4·55	4·8
$C_{10}H_{14}$	75·12	74·8	5·44	5·5

The Cedrenes.

Some of the essential oils contain hydrocarbons of the same empirical composition as the terpenes or citrenes, but differing from them considerably in physical properties. They are less limpid at the ordinary temperature, the specific gravity and boiling point are both higher, they do not expand so much when heated, and are sparingly soluble in alcohol. Their vapour-density points to the molecular formula $C_{15}H_{24}$. The average properties of nine specimens in the original list, including cloves, rosewood, cubebs, calamus, cascarilla, and patchouli, all fairly accordant, are as follows. As the hydrocarbon from patchouli seems to be a very pure cedrene, and I happen to have examined three different specimens, the mean of them is given in the second column :—

	All.	Patchouli.
Boiling point	249° to 260°	254° to 260°
Specific gravity at 20° C.	0·9173	0·9251
Refractive index for A	1·4944	1·4979
Dispersion.....................	0·0293	0·0270
Specific refractive energy.......	0·5390	0·5384
Specific dispersive energy.......	0·0319	0·0292

These figures agree fairly well with a specimen of cedrene from cedar, more recently determined (Trans., 1884, 248), viz., specific refractive energy 0·5377, and specific dispersive energy 0·0299. It appears, therefore, that the cedrenes closely resemble the terpenes in their optical properties, and they must be considered polymeric with that group. None of the specimens examined were in fact as refractive as the citrenes.

The following will be the equivalents calculated out, and compared with polymerised terpene :—

* Kanonnikoff determined the refraction equivalent of his "tetrahydroterpene," $C_{10}H_{20}$, at 76·6 for the line C, which corresponds well with the above for the line A.

Cedrenes.	Refraction equivalent.		Dispersion equivalent.	
	Found.	Calculated.	Found.	Calculated.
Old observations (mean)	109·9	109·5	6·51	6·06
From patchouli "	109·8	"	5·96	"
From cedar................	109·7	"	6·10	"

To this view it may be objected that no graphic formula can be framed for $C_{15}H_{24}$, containing $1\frac{1}{2}$ pair of carbon-atoms doubly-linked. It must be remembered, however, that our numerical formulæ are founded on the volume in the gaseous condition, and that we really know nothing of the molecular volume of liquids. All that we can deduce from the experiment is that the liquid terpenes and cedrenes are polymeric in the strictest sense of the term, but what multiple of $C_{10}H_{16}$ either of them may be is beyond our conjecture at present.

Caoutchene.

Among the juices of plants which are supposed to contain a substance of the composition $C_{10}H_{16}$ is caoutchouc, and so peculiar are the qualities of this substance that it seemed desirable to examine, if possible, its optical properties. Unfortunately I have not yet succeeded in isolating a hydrocarbon which can be depended on as being free from oxygen, and pure, but several preparations have been made from good white caoutchouc by soaking it for some time in chloroform and fractionally precipitating the dissolved portion by means of alcohol. The first fractions thrown down were a viscid substance, which, when dissolved in benzene, gives a specific refractive energy which varies rather widely in different specimens, but averages about 0·55. The specific dispersive energy is about 0·037, and this suggests the presence of two pairs of doubly-linked carbons. Indeed there is some evidence of the existence of a substance having a still higher dispersive power.

Caoutchene, the liquid $C_{10}H_{16}$, obtained by the dry distillation of india-rubber, has a boiling point and specific gravity similar to those of citrene. A specimen that boiled between 172° and 178° yielded the numbers given in the Appendix, from which may be deduced the specific refractive energy of 0·554, and the specific dispersive energy of 0·0366, giving—

	Observed.	Calculated.
Refraction equivalent	75·33	75·2
Dispersion equivalent	4·98	4·84

In these optical properties, therefore, caoutchene also appears to be a citrene.

Isoprene.

It is interesting to compare with these hydrocarbons another liquid, derived from similar sources, having the same composition, but a smaller molecular weight. Through the kindness of Dr. Tilden, I have examined his specimens of pentine, derived by heat from turpentine, and isoprene, by the dry distillation from caoutchouc, both of which have the formula C_5H_8. The observations are given in the Appendix, from which the following data are calculated :—

	Sp. refractive energy.	Sp. dispersive energy.
Pentine............	0·5922	0·0479
Isoprene	0·5922	0·0460

This practical identity in optical properties confirms Dr. Tilden's opinion (Trans., 1884, 410) that the two substances are the same, and the figures show them to be entirely distinct from both terpenes and citrenes. It is necessary to conclude that no less than four of the five carbon-atoms are doubly-linked, which would give—

	Found.	Calculated.
Refraction equivalent	40·27	39·8
Dispersion equivalent	3·19	3·22

This is in accordance with the conclusion of Tilden based on the fact that they combine with four atoms of bromine, or 2 mols. HCl.

Chemical Structure.

If it be true that the amount of carbon doubly-linked varies in different members of this isomeric group of hydrocarbons, it goes far to explain the divergence in their properties. The differences in their molecular structure must indeed be very important. Isoprene would have to be expressed in a graphic formula by an open chain, while the citrenes and caoutchene must be represented by means of a closed chain; and terpene and camphene by some kind of double ring. The great readiness with which cymene may be derived from the various $C_{10}H_{16}$'s, has led chemists generally to believe that these compounds are allied to the aromatic compounds; this is confirmed by their optical properties, and the formula suggested by Kekulé, Fig. 1, may be retained for the citrenes, but it must be modified for the camphenes and terpenes. The most symmetrical arrangement would be that of Fig. 2; but Armstrong and Kanonnikoff have

already suggested graphic formulæ which are intended to express the chemical reactions more fully, and either of which would meet the requirements of the optical observations.

FIG. 1.

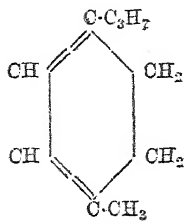
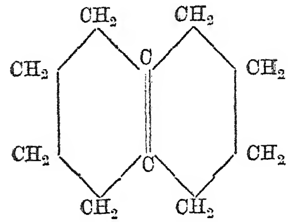


FIG. 2.



Another cause of difference in these and isomeric compounds may possibly be indicated by a peculiarity of their dispersion equivalents. It is found, as already stated, that the double linking, in the allyl compounds for instance, affects the dispersion to a much smaller degree than in the aromatic bodies, and it may eventually prove that there is a similar cause for the smaller dispersion observed in the case of camphene and the citrenes. This points to some difference of structure hitherto unrecognized; but it can as yet be viewed only as a speculation.

Other Optical Evidence.

The phenomena of refraction and dispersion are not the only ways in which light may reveal to us the structure of these hydrocarbons. The phenomena of absorption also give us indications. Thus Hartley shows (*Proc. Roy. Soc.*, 1879, 290), that terpenes and citrenes absorb the ultra-violet rays to a considerable extent, that cedrenes absorb them to a still greater degree, but that neither they nor their hydrates and oxides show the phenomena of selective absorption characteristic of the aromatic group which contain three pairs of carbon-atoms doubly-linked, and which is strongly marked wherever cymene is present.

Abney and Festing (*Phil. Trans.*, 1881, Plate 88) have examined the absorption of the infra-red part of the spectrum by some of the same substances, and here again the peculiar selective absorption which characterises the members of the benzene-group is not shown by oil of turpentine. But there are other absorption-bands; and Captain Abney informs me that judging from his observations on several of the essential oils and their congeners, he would consider that they are rather of the nature of the aromatic than of the fatty acid compounds.

Oxygen Compounds.

I had intended discussing the oxygen compounds in a similar manner; but the subject presents great difficulties, arising partly from the difficulty of obtaining these compounds in a sufficiently pure condition, and partly from the double function of oxygen. Thus, to take a special instance. Citronellol probably has the formula $C_{10}H_{18}O$, but the separation of it from other compounds contained in the crude oil is extremely difficult. It is evident also that the atom of oxygen may occupy the position either of that in alcohol or of that in acetone. In the one case there would be one pair of doubly-linked carbon-atoms more than in the other. The matter is complicated by the fact that the oxygen would not have the same refraction equivalent in the two cases. Where joined by single bonds it has the value 2·8, and where joined by double bonds 3·4, according to Brühl. I find a similar difference in the dispersion equivalent, the respective values being very wide apart, viz., about 0·10 and 0·18. I may return to this subject some day; in the meantime I will content myself with stating two or three conclusions that may be looked upon as fairly established.

1st. Camphor, although its composition is $C_{10}H_{16}O$, has the optical properties of a saturated compound, thus confirming the view which has been entertained from its chemical properties. This suggests its close relationship to the terpenes.

2nd. Besides camphor ($C_{10}H_{16}O$), cajeputol and its isomerides ($C_{10}H_{18}O$), and menthol ($C_{10}H_{20}O$), have the refractive and dispersive energy of saturated compounds. This gives much room for speculation as to the differences between their constitutional formulæ.

3rd. Conversely, isomeric compounds containing oxygen may have a different refractive energy. Thus terpinol ($C_{10}H_{18}O$), unlike cajeputol, is shown both by its refractive and dispersive energy to have one pair of doubly-linked carbon-atoms. Or to take $C_{10}H_{14}O$, carvol appears to have two pairs of doubly-linked carbon-atoms, while thymol has certainly three.

4th. Anethol ($C_{10}H_{12}O$), belongs to another category. Its refractive and dispersive energy are both too great to be explained by the supposition of four pairs of carbon-atoms doubly-linked.

Since the foregoing was drafted, Kanonnikoff has sent me a copy of his paper in the *Journal für praktische Chemie*, **33**, 497, in which I find that he discusses several of these oxygen compounds from the point of view of their refraction equivalents, and has arrived mainly at the same results.

Summary.

The preceding discussion may be summarised as to its main results in the following table. Instead of repeating the refraction and dispersion equivalents, I have preferred returning to the specific refractive and dispersive energy. These numbers represent experimental facts whatever the theory may be about the substance examined, independent even of its composition. They are given in columns 2 and 3, while the figures deduced from my theory in regard to each of the hydrocarbons are given in columns 5 and 6. That theory is expressed in column 4, which contains the number of pairs of carbon-atoms that I take to be in a "doubly-linked" condition, on the basis of each substance containing 10 atoms of carbon. Whether in fact it is C_{10}, or C_{15}, or C_5, is not indicated by these optical properties, but rests solely on other evidence. In estimating the value of the figures, it must be remembered that the physical observations are trustworthy to the third, if not the fourth, place of decimals, those for dispersive energy being somewhat more exact than those for refractive energy; but the same amount of accuracy cannot of course be attained in respect of the chemical purity of the different substances.

Hydrocarbon.	Experimental		Pairs of C doubly-linked.	Theoretical	
	Specific refractive energy.	Specific dispersive energy.		Specific refractive energy.	Specific dispersive energy.
Cymhydrene	0·543	0·0246	none	0·543	0·0243
Menthene	0·548	0·0313	one	0·547	0·0298
The terpenes	0·537	0·0295	,,	0·537	0·0296
Terebenthene	0·537	0·0294	,,	,,	,,
Camphene............	0·528	0·0269	,,	,,	,,
The cedrenes	0·538	0·0296	,,	,,	,,
The citrenes	0·551	0·0334	two	0·553	0·0354
Isoterebenthene........	0·552	0·0337	,,	,,	,,
Caoutchene............	0·554	0·0366	,,	,,	,,
Cymene	0·560	0·0406	three	0·558	0·0413
Isoprene	0·592	0·0470	four	0·585	0·0472

The advance in these experimental figures with the double linking is evident enough, though it is obscured in the first two lines by the larger amount of hydrogen contained in cymhydrene and menthene. The influence of the double linking upon the specific dispersive energy is apparent at a glance, and renders this property more valuable than the refractive energy in determining the rational con-

stitution; though of course it is in the agreement of the two that we may seek the most conclusive evidence.

Appendix.

The indices made use of in this paper, and not previously published, are given in the following table. The specimens of pentine, isoprene, and terpinol were kindly lent me by Professor Tilden; the sage-terpene by Mr. Pattison-Muir, and the artificial anethol by Dr. Perkin. Fresh determinations of cymene, carvol, and anethol are added.

Substance.	Temp. C.	Specific gravity.	Refractive indices.		
			μ_A.	μ_D.	μ_H.
Terpene from pine......	10·2°	0·8711	1·4683	1·4742	1·4939
„ sage......	24·5	0·8632	1·4611	1·4667	1·4855
„ mint.....	17·3	0·8646	1·4635	1·4696	1·4891
Cymene..............	21	0·8551	1·4759	1·4835	1·5083
Caoutchene...........	16	0·8449	1·4680	1·4750	1·4989
Pentine..............	18	0·6766	1·4007	1·4079	1·4331
Isoprene.............	18	0·6709	1·3973	1·4041	1·4282
Terpinol.............	10	0·9296	1·4770	1·4838	1·5026
Carvol...............	11	0·9667	1·4940	1·5020	1·5298
Anethol..............	21	0·9869	1·5464	—	1·6167
„ artificial.......	21	0·9870	1·5474	1·5614	1·6174

The refraction and dispersion equivalents of the oxygen compounds in the above table, together with a new determination of thymol dissolved in alcohol, are:—

Terpinol	79·02	and	4·23
Carvol	76·68	„	5·53
Thymol...............	78·91	„	6·38
Anethol (natural)	81·93	„	10·56
„ (artificial)....	82·08	„	10·49

LVIII.—*A Method of Investigating the Constitution of Azo- and Diazo-derivatives and Analogous Compounds.*

By Raphael Meldola, F.R.S., Professor of Chemistry, and F. W. Streatfeild, Demonstrator of Chemistry in the Finsbury Technical College, City and Guilds of London Institute.

In former papers by one of the authors (Meldola, Trans., 1883, 436, and 1884, 117), it was pointed out that the compounds resulting from the action of diazo-salts of para- and meta-nitraniline on β-naphthylamine possessed neither the characters of true azo- nor diazo-compounds, and it was suggested that these substances might be related to the class of azimido-compounds of which the simplest representative is Griess's azimidobenzene:—

$$C_6H_4{<}\begin{matrix}N\\ |\\ N\end{matrix}{>}NH.$$

According to this view, the general formula of these compounds may be written—

$$X{<}\begin{matrix}NH\\ NH\end{matrix}{>}N\cdot Y,$$

where X and Y may be similar or dissimilar, and the compounds may be regarded as derivatives of the typical hydrazimido-compounds:—

$$X{<}\begin{matrix}NH\\ NH\end{matrix}{>}NH.$$

In the paper referred to, it was further suggested that the difference in the constitution of these β-naphthylamine compounds resulted from the interaction of the azo- and amido-groups, which in all probability occupy an ortho-position with respect to one another, so that the investigation of the supposed azo-compounds derived from orthamido-compounds becomes a matter of considerable importance. The necessity of continuing the investigation in this direction has always been kept in view, although, since the publication of the paper in question, much additional evidence has been gained by the researches of Zincke and his pupils (*Ber.*, 1885, 3132 and 3142; Lawson, *ibid.*, 796 and 2422, and *Inaug. Diss.*, Marburg, 1885; Sachs, *Ber.*, 1885, 3125).

Among the recent results, the most important in relation to the constitution of the compounds under consideration is undoubtedly the discovery that they can be oxidised to substances of the azimido type (Zincke, *Ber.*, 1885, 3134). Upon this evidence Zincke accepts the

conclusion which had been arrived at on other grounds in the paper published in the Transactions of this Society in 1884, viz., that the compounds in question no longer contain an amido-group, but two NH-groups. With respect to the constitution of these compounds Zincke gives the two formulæ—

$$X{-}N\Big\langle{}^{NH}_{NH}\Big\rangle Y, \qquad X{-}NH\Big\langle{}^{HN}_{N}\Big\rangle Y,$$

I. II.

the first of these corresponding with that proposed by one of the authors of the present paper in 1884, and the second corresponding with the formation of β-naphthaquinone-hydrazide from β-naphthaquinone and phenylhydrazine as observed by Zincke and Bindewald (*Ber.*, 1884, 3026):—

$$C_{10}H_6O_2 + H_2N{\cdot}NH{\cdot}C_6H_5 = C_{10}H_6\Big\langle{}^{O(\alpha)}_{N\cdot NH\cdot C_6H_5} + OH_2.$$

The evidence at present available does not render it possible to decide between these formulæ, and further investigation therefore appears necessary.

In a note published by one of the authors (Meldola, *Chem. News*, Dec. 5, 1884), it was suggested among other methods of investigating the constitution of these and analogous compounds, that the behaviour of the alkyl-derivatives, on reduction, might throw light on the question. Thus, with respect to the two formulæ given, a monalkyl-derivative of I would give, on complete reduction, $X{\cdot}NH_2$ and $NH{\cdot}Y{\cdot}NR$; and a monalkyl-derivative of II would give either $X{\cdot}NHR$ and $NH_2{\cdot}Y{\cdot}NH_2$ or $X{\cdot}NH_2$ and $NH_2{\cdot}Y{\cdot}NR$, according to the position of the radicle. A dialkyl-derivative of I would give on reduction $X{\cdot}NH_2$ and $NR{\cdot}Y{\cdot}NR$, and of II, $X{\cdot}NHR_2$ and $NH_2{\cdot}Y{\cdot}NHR$. The same considerations evidently apply to diazoamido- and amidoazo-compounds, and, as far as we are aware, the decomposition products of the alkyl-derivatives of these compounds have not hitherto been investigated. Thus mono- and di-alkyl-derivatives of true amido-azo-compounds of the type $X{\cdot}N_2{\cdot}Y{\cdot}NH_2$ would give on reduction $X{\cdot}NH_2$ and $NH_2{\cdot}Y{\cdot}NHR$, or $NH_2{\cdot}Y{\cdot}NR_2$, whilst diazoamido-compounds of the type $X{\cdot}N_2{\cdot}NH{\cdot}Y$ could only give monalkyl-derivatives, $X{\cdot}N_2{\cdot}NR{\cdot}Y$, which, on reduction, would yield $X{\cdot}NH_2$ and $Y{\cdot}NHR$.

It appeared also that the present method would be capable of determining finally the question of the symmetrical or asymmetrical formula of the diazoamido-compounds. The symmetrical formula for diazobenzeneanilide—

$$HN\Big\langle{}^{N\cdot C_6H_5}_{N\cdot C_6H_5},$$

is given by Victor Meyer (*Ber.*, 1881, 2447), but is rejected by him as having little probability. The same formula has recently been brought forward by Friswell and Green (Trans., 1885, 924), who state that it appears to them to be more probable than the asymmetrical formula. Supposing the diazo-amido-compounds to have the symmetrical formula above given, it is evident that their monalkyl-derivatives on reduction would give $X\cdot NH_2, Y\cdot NH_2$ and NRH_2.

In order to apply the present method, ethyl iodide was used as the exploring agent, and, although we have as yet only studied one compound, the results are sufficiently interesting to warrant their being communicated to the Society.

We propose to extend the investigation to other diazo-, azo-, azimido-, and oxyazo-compounds.

Paradinitrodiazoamidobenzene.

In the present communication, we give the results of the application of the method indicated to the above-named substance, which has not hitherto been prepared, the only analogous compound at present known being the supposed dinitrodiazoamidobenzene obtained by Hallman by the action of nitrous acid on metanitraniline (*Ber.*, 1876, 390). We propose to apply our method to Hallman's compound at an early opportunity. In starting from paranitraniline for our first experiments, we had two objects in view.

In the first place it appeared probable that the compounds resulting from the action of nitrous acid on the nitranilines would be of a distinctly acid character owing to the presence of the nitro-groups, thus offering the possibility of easy displacement of H by alkyl radicles in NH-groups which might be present, since the acidity of the molecule rendered it probable that the H in the NH-group would be displaceable by metals, and the salts thus formed would be decomposable by alkyl iodides, &c. In the next place, in the case of paranitraniline, where the para-position with respect to the NH_2-group is occupied, it appeared probable that a true diazo-compound would in the first place be formed, and that if this could be transformed into its isomeric amido-azo-compound the N_2-group would occupy the ortho-position with respect to the amido-group. Thus there might be formed one of the compounds represented by the following formulæ:—

$$\underset{(4)}{NO_2}\cdot C_6H_4\cdot \underset{(1)}{N_2}\cdot \underset{(1)}{NH}\cdot C_6H_4\cdot \underset{(4)}{NO_2}, \qquad \underset{(4)}{NO_2}\cdot C_6H_4\cdot \underset{(1)}{N} : \underset{(2)}{N}\cdot C_6H_3(\underset{(4)}{NO_2})\cdot \underset{(1)}{NH_2},$$

I. II.

$$NO_2\cdot C_6H_4\cdot N\left\langle{NH \atop NH}\right\rangle C_6H_3\cdot NO_2, \qquad NO_2\cdot C_6H_4\cdot NH\left\langle{HN \atop N}\right\rangle C_6H_3\cdot NO_2.$$

III. IV.

As the result of our experiments, we find that with paranitraniline a true diazo-amido-compound (formula I) is alone produced.

In order to prepare this substance, paranitraniline was dissolved in the minimum quantity of strong hydrochloric acid, and the cold solution diluted with water, but not so much as to throw out the nitraniline. The solution of sodium nitrite (1 mol. to 2 mols. nitraniline) was then gradually added, and the mixed solutions allowed to remain in a cool place for 12—14 hours. The separation of the diazo-compound commenced when the whole of the nitrite had been added, and at the expiration of the time mentioned the contents of the flask had become semi-solid. The pulpy yellow precipitate was collected, washed thoroughly with cold water, and a specimen purified for analysis by crystallisation from alcohol. It forms small yellow needles soluble in boiling alcohol and acetone, but not very readily, and only sparingly soluble in chloroform and the benzene hydrocarbons. It melts at 223°, at the same time frothing up and decomposing. The following results were obtained on analysis:—

I. 0·1346 gram gave 0·2489 gram CO_2 and 0·0372 gram water.

II. 0·0843 gram burnt in a vacuum with CuO gave 17·8 c.c. N at 15·5°, and 760·1 mm. bar.

	Theory for $NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}NH{\cdot}C_6H_4{\cdot}NO_2$.	Found.
C.........	50·17	50·43
H.........	3·13	3·07
N.........	24·39	24·66

The substance, as anticipated, possesses distinctly acid properties, dissolving in cold alcoholic potash or soda with a splendid magenta-red colour, and in boiling aqueous alkalis with a similar colour. The alkaline solutions show a remarkable stability, the substance forming well characterised crystalline salts which separate out from the solutions on cooling. The sodium salt, which probably has the formula $NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}NNa{\cdot}C_6H_4{\cdot}NO_2$, forms beautiful steel-blue needles, but these are stable only in the presence of excess of alkali; when collected and washed, they gradually decompose on exposure to the air with the liberation of the original yellow substance. The acidity of the substance is sufficiently great to decompose alkaline carbonates, the characteristic red colour being developed on boiling the diazo-compound with a solution of potassium or sodium carbonate. The stability of the substance in the presence of alkalis was shown by boiling some of it for two days with an excess of strong caustic potash solution; the crystalline potassium salt, on being decomposed by dilute sulphuric acid, gave the original substance unaltered. The cold alkaline solution of the compound, when acidified, gives the

original substance in the form of a greenish gelatinous precipitate which gradually becomes yellow on standing; on acidifying the hot alkaline solution, the substance immediately separates in a yellow flocculent state. It is very unstable in the presence of acids, being decomposed by boiling with glacial acetic acid with evolution of nitrogen and the formation of resinous uncrystallisable products. Heated with dilute sulphuric (1 part strong acid to 4 of water) in a sealed tube for 2—3 hours at 100°, the substance is decomposed with the liberation of nitrogen and the formation of paranitraniline and resinous products. No nitrophenol appears to be formed in this reaction. A similar decomposition was effected by heating the substance with water in a sealed tube at 230° for three hours, the product being, as before, paranitraniline and resin.

Products of Reduction.

Supposing the substance to have been an amidoazo-compound, it seemed advisable to study in the first place the action of mild reducing agents in order to see whether a hydrazo-compound could be obtained. By the action of ammonium sulphide on a warm alcoholic solution of the sodium salt, reduction was effected and the magenta-red colour of the solution gradually changed to orange. On dilution with water, a reddish flocculent substance separated out, but this did not appear to be a very definite compound, as it could not be crystallised, and had no definite melting point. It decomposes when heated, and a specimen that had been placed to dry in the water-oven suddenly frothed up and decomposed with carbonisation. The dry substance forms a reddish powder which deflagrates vigorously on ignition. We have since found that more satisfactory results are obtained by reducing the hot aqueous solution of the sodium salt with ammonium sulphide. When the red colour of the solution has disappeared, reddish-brown needle-shaped crystals are deposited on cooling. We propose to make a further study of this reduction product, but the main question of the constitution of the original substance is for the present settled by the fact that on complete reduction it gives only paraphenylenediamine. This was proved by a careful examination of the reduction products obtained by the action of zinc-dust and acetic acid and of tin and hydrochloric acid on the compound dissolved in alcohol. In both cases, paraphenylenediamine was the sole product, and was identified by its characteristic colour reactions with ferric chloride, potassium dichomate, ferric chloride in the presence of hydrogen sulphide, and by the analysis of the diacetyl-derivative. The formulæ II, III, and IV are thus excluded, as these substances on reduction would give a mixture of di- and tri-amidobenzenes, and the substance is therefore a true diazoamido-compound.

Decomposition by Hydrochloric Acid.

When decomposed by heating with acids in the presence of water, diazoamido-compounds usually break up into amido-derivatives, phenols, and nitrogen. It appears, however, from Lawson's experiments (*Ber.*, 1885, 797) that this mode of decomposition is not confined to diazoamido-compounds, since the compounds obtained by the action of diazotised amines on β-naphthylamine also yield the amine (β-$C_{10}H_7 \cdot NH_2$) and the corresponding phenol ($C_6H_5 \cdot OH, NO_2 \cdot C_6H_4 \cdot OH$, &c.). That these β-naphthylamine compounds are not true diazoamido-compounds is shown by the fact that they give naphthylenediamine on reduction.* The failure to obtain nitrophenol from the present dinitrodiazoamidobenzene by decomposing it with dilute sulphuric acid is thus a feature in the character of the diazoamido-compounds to which it seems desirable to call special attention. Much more definite results were obtained by decomposing the substance with strong hydrochloric acid, three hours' heating in a sealed tube in a water-bath being sufficient for complete decomposition. Nitrogen is given off on opening the tube, the contents consisting of a mixture of large needle-shaped crystals and a dark tarry substance, together with the excess of acid liquid. The crystals were identified as the hydrochloride of paranitraniline, and the tarry substance, after being repeatedly washed with warm dilute hydrochloric acid to completely remove the paranitraniline, was found to be separable by steam distillation into a white crystalline substance having an odour of bitter almond oil, and a small quantity of a dark oil which remained behind in the flask and solidified on cooling to a brittle resin. The crystalline distillate was purified by redistillation in a current of steam, and proved to be paranitrochlorobenzene: m. p. 83°:—

0·1737 gram burnt with lime gave 0·1590 gram AgCl.

	Theory for $C_6H_4 \cdot Cl \cdot NO_2$.	Found.
Cl......	22·54	22·63

The decomposition of the diazoamido-compound by hydrochloric acid may thus be simply represented by the equation—

$$NO_2 \cdot C_6H_4 \cdot N_2 \cdot NH \cdot C_6H_4 \cdot NO_2 + HCl = NO_2 \cdot C_6H_4Cl + N_2 + NH_2 \cdot C_6H_4 \cdot NO_2.$$

It seems most probable that the nitraniline residue to the left of the N_2-group in the above formula, that is the nucleus directly

* According to a recent paper by Nietzki and Goll (*Ber.*, 1886, 1281), amido-azo-β-naphthalene can be diazotised under suitable conditions, and thus appears to contain an NH_2-group.

attached to the azo-group, is the one into which the chlorine of the acid enters to displace the N_2.

This point is, however, sufficiently interesting to examine into further, as it is by no means certain that intramolecular rearrangement may not occur during the decomposition of diazo-compounds, owing to the formation of intermediate additive products. We propose to extend our investigations in this direction by examining the decomposition products of mixed diazoamido-compounds containing dissimilar radicles.

Paradinitrodiazoethylamidobenzene.

In order to prepare this compound, the dinitrodiazoamidobenzene was dissolved in alcohol with the addition of the theoretical quantity of caustic potash to form the potassium salt. The necessary quantity of ethyl iodide was then added and the liquid kept boiling in a flask with an upright condenser for about 10 hours, when the red colour of the solution had disappeared and a heavy yellowish crystalline deposit had separated: 20 grams of the dinitrodiazo-compound gave about 18 grams of the ethyl-derivative, or about 81 per cent. of the theoretical quantity. The ethyl-derivative was collected, washed with water to remove potassium iodide, and crystallised twice from alcohol in which it is but very sparingly soluble. The substance forms small yellow needles, melting without decomposition at 191—192°.

I. 0·2825 gram gave 0·5501 gram CO_2 and 0·1072 gram OH_2.
II. 0·1456 gram gave 0·2845 gram CO_2 and 0·0550 gram OH_2.
III. 0·0958 gram burnt into vacuum with CuO gave 17·9 c.c. N at 13·7° and 757 mm. bar.

	Theory for $NO_2\cdot C_6H_4\cdot N_2\cdot N(C_2H_5)\cdot C_6H_4\cdot NO_2$.	Found. I.	II.	III.
C	53·33	53·11	53·28	—
H	4·12	4·21	4·19	—
N	22·22	—	—	21·9

The ethyl-derivative is no longer soluble in alkalis, thus confirming the view that the salt-forming power of the original substance is due to the hydrogen of the $-N_2\cdot NH-$ group. The compound is quite as unstable towards acids as the original substance, being decomposed by glacial acetic acid, dilute sulphuric acid, &c., but, as before, no nitrophenol is formed. The decomposition with hydrochloric acid was effected by heating in a sealed tube in a water-bath for 2 to 3 hours. The products of this reaction proved to be paranitrochlorobenzene and ethylparanitraniline:—

$$NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}N(C_2H_5){\cdot}C_6H_4{\cdot}NO_2 + HCl = NO_2{\cdot}C_6H_4Cl + N_2 + NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}C_2H_5.$$

The last-named compound, which was first described by Weller (*Ber.*, 1883, 31), was identified by its melting point (95—96°) and crystalline form, as well as by the analysis of its nitroso-derivative which has not been hitherto described.

Ethylparanitrophenylnitrosamine, $NO_2{\cdot}C_6H_4{\cdot}N(NO){\cdot}C_2H_5$.—On adding the necessary quantity of sodium nitrite dissolved in water to the hydrochloric acid solution of ethylparanitraniline, a white flocculent precipitate of the nitrosamine at once separates. This was collected, washed with water, and crystallised from alcohol. It forms large straw-coloured needles melting at 119·5°. The corresponding ethylmetanitrophenylnitrosamine melts at 47° (Nölting and Stricker, *Ber.*, 1886, 546).

The decomposition of the ethyl-derivative by hydrochloric acid into ethylnitraniline and nitrochlorobenzene is conclusive evidence against the symmetrical formula—

$$C_2H_5{\cdot}N\langle\begin{array}{l}N{\cdot}C_6H_4{\cdot}NO_2\\ |\\ N{\cdot}C_6H_4{\cdot}NO_2\end{array}.$$

We have not yet applied the present method of investigation to the simpler unsubstituted diazoamido-compounds, but we have no doubt that it will be found generally applicable. Alkyl-derivatives of such diazoamido-compounds have however been prepared by Gastiger (*Bull. Soc. Chim.*, **42**, 338) and by Nölting and Binder (*ibid.*, **42**, 336 and 341), by acting with diazobenzene and paradiazotoluene chloride on ethylaniline. The resulting compounds have the formulæ $C_6H_5{\cdot}N_2{\cdot}N(C_2H_5){\cdot}C_6H_5$, $CH_3{\cdot}C_6H_4{\cdot}N_2{\cdot}N(C_2H_5){\cdot}C_6H_5$, &c., and behave as true diazoamido-compounds when decomposed by acids, the products being phenol and ethylaniline, and paracresol and ethylaniline respectively.

As the results of this investigation showed that the substance obtained by the action of nitrous acid on paranitraniline is a true diazoamido-compound, an attempt was made to convert it into its isomeric amidoazo-compound by dissolving it in fused paranitraniline containing paranitraniline hydrochloride. Under these circumstances, however, complete decomposition takes place with the evolution of nitrogen and the formation of an uncrystallisable resinous substance.

LIX.—*The Formation and Destruction of Nitrates and Nitrites in Artificial Solutions and in River and Well Waters.*

By J. H. M. Munro, D.Sc., College of Agriculture, Downton, Salisbury.

CONTENTS.

In the spring of 1883, attracted by MM. Schloesing and Müntz's account of the nitrifying organism of the soil, and by Mr. R. Warington's extremely interesting researches on "Nitrification," which had been published in the *Journal of the Chemical Society* (Trans., 1878, 44, and Trans., 1879, 429), I commenced a few observations on the same subject. My first series of experiments was commenced before I became acquainted with Mr. Warington, and indeed, without the knowledge that he was pursuing his investigations on this subject. This series was designed to repeat and corroborate some of Mr. Warington's observations with ammonium salts, and to extend the results to three or four other nitrogenous compounds. Later on, I communicated with that gentleman, and received from him advice derived

from his own experience, and encouragement to pursue my observations with the view of eliciting new facts.

So slow, however, is the nitrifying process under some conditions, that this first series remained under observation for nearly two years, whilst subsequent nitrifying solutions, started in the summer and autumn of 1883, are only just done with. The great length of time occupied in these experiments is perhaps the reason why so few English chemists appear to have been attracted to the subject. Under these circumstances observations which corroborate the statements of others have some value, and in accordance with Mr. Warington's wish, I now condense into a brief form such of my results as appear of any interest, in view of the continuation of his researches (Trans., 1884, 637), together with some experiments on substances other than ammonium salts, on nitrification in natural waters, and on denitrification, which I believe to be original. The observations now described were made in 1883 and the spring of 1884, that is, between the publication of Warington's second (1879) and third (1884) reports; the only exceptions are certain experiments which I have made within the last two months, to elucidate points which occurred to me during the preparation of the paper for publication.

To attain as much clearness as possible, I have arranged the experiments in something like chronological order under separate headings, and will consider in succession—

Nitrification of Nitrogenous Compounds other than Ammonium Salts.
Nitrification of Ammonium Salts in Artificial Solutions.
Nitrification of Ammonium Salts in Well and River Waters.
Denitrification, and the Influence of Organic Matter on Nitrification.

I. *Nitrification of Ethylamine by Soil.*

We have direct and conclusive evidence that plants avail themselves of nitrogen supplied as nitrates, and that the nitrates are absorbed as such by the plants, and in some cases stored up without immediate alteration in their tissues. Taking into consideration with this the fact that all organic manures evolve ammonia during decomposition, and that ammonia in the soil is rapidly transformed into a nitrate, it may well be doubted whether plants ever assimilate nitrogen directly from any other compounds than nitrates. It was for this reason that it seemed to me interesting to ascertain whether ethylamine is nitrified by contact with soil, for G. Ville has long ago shown (*Recherches sur la Végétation,* 1857) that ethylamine and ammonia are equally efficacious as nitrogenous manures. Trimethylamine has also been successfully tried as a manure in France.

The sample of ethylamine hydrochloride employed was tested for purity by conversion into aurochloride. The crystals of ethylammonium aurochloride on ignition gave 50·78 per cent. metallic gold, whereas the formula $C_2H_5{\cdot}NH_3Cl,AuCl_3$ requires 51·04 per cent.

I experimented in all with three solutions of ethylamine hydrochloride. Two of these were made up on March 9, 1883, and the description of the mode in which they were prepared and examined applies to all the solutions of my first series, to which the same date is affixed. The modifications adopted in later series are noticed in their place.

309 mgrms. (B1) and 618 mgrms. (B2) ethylamine hydrochloride were dissolved in ammonia-free distilled water in two stoppered bottles, to each of which I then added—

222 mgrms. potassium hydrogen tartrate,
222 „ magnesium sulphate, cryst.,
222 „ sodium phosphate, cryst.,

and water to 500 c.c. Half a teaspoonful of precipitated calcium carbonate to render the mixture permanently alkaline, and 2 grams moist arable soil, were put in afterwards. All the solutions of this date were kept in stoppered or corked bottles or flasks, about half full, which were placed in a cupboard in the laboratory, and exposed to the ordinary variations of temperature of the place. Chiefly on account of the low temperature prevailing, nitrification did not take place in any of the solutions of this series until the beginning of June, but when once commenced, it proceeded in several cases with great rapidity. The solutions were examined from time to time, for *ammonia* by the Nessler reagent, for *nitrites* by permanganate, and for *nitrates* or *nitrites* by the indigo test as used by Boussingault. It was only in later experiments that I adopted the more delicate reagents, metaphenylenediamine and diphenylamine, in place of permanganate and indigo for qualitative testings. The quantitative determinations were made as follows:—

Ammonia, by Nesslerising a diluted fraction of the liquid.

Nitrites, by weak standard permanganate (1 c.c. = 0·0001 gram available oxygen) in a pipetted fraction of the liquid acidified with sulphuric acid.

Nitrate in absence of nitrite, by the indigo process as modified by Warington.

Nitrate in presence of nitrite, by oxidising the nitrite in a pipetted fraction by cautious addition of permanganate, then determining the total nitrate with indigo, and deducting the nitrate formed from nitrite.

These methods, which are the same as those used by Warington,

enable one to follow very fairly the progress of a nitrifying solution, but they do not yield results of great accuracy. In some of my later experiments, for example, I wished to ascertain whether the nitrification was *solely* nitrous, or whether a small quantity of nitrate coexisted with the nitrite, and this it was extremely difficult to do, if not impossible. The estimations of ammoniacal nitrogen are merely approximate in all cases, since any error made in Nesslerising the very small fraction of liquid available for each testing is greatly multiplied when calculated on the whole 500 c.c.

The progress of the solutions B1 and B2 is recorded in the summary of observations made at the following dates:—

B1.—Made up March 9, 1883. 500 c.c. contained 309 mgrms. ethylamine hydrochloride = 53 mgrms. nitrogen. No ammonia, nitrites, or nitrates, were detected up to March 26. Between this and April 13, however, the solution became turbid, small patches of mycelium began to appear throughout the liquid, and ammonia was formed. By July 11 the ammonia present amounted to 16 mgrms. nitrogen, and nitrate was present. On July 26 the N as nitrite amounted to 28 mgrms., but between this date and August 16 it was completely converted into nitrate. Nitrification was practically complete on this date, and the N present as nitrate was estimated as $47\frac{1}{2}$ mgrms., or 90 per cent. of that originally taken.

B2.—Made up March 9, 1883, was double as strong as the preceding, and contained 106 mgrms. N in 500 c.c. For a time this followed a similar course to B1. On July 11 the ammonia present was equivalent to 33 mgrms. nitrogen, and the nitrous fermentation proceeded with such rapidity from this date, that by July 26 *all* the nitrogen was present as nitrite (105 mgrms. estimated). Instead of suffering conversion into nitrate by August 18, however, the nitrite was quite unaltered on that date, the quantity of permanganate consumed being exactly the same as before. Conversion into nitrate set in some time during the long vacation, for on October 18 *no* nitrite was present, and the N as nitrate was estimated as 104 mgrms., again over 90 per cent. of that originally present as ethylamine.

These two experiments show that ethylamine is easily nitrified, and that the process is divisible into three stages. At first ammonia is produced, and this may suffer total conversion into nitrite before any nitrate is formed (B2); the nitrite may be rapidly converted into nitrate, or may persist for a time without alteration (B2), ultimately, however, undergoing complete oxidation. The apparently capricious persistence of nitrite, ending sometimes in sudden and rapid conversion into nitrate, occurred in many of my experiments, as well as in those of Warington.

The third solution of ethylamine was made up on July 20, 1883,

and belongs to a series of mixtures nearly all of which failed to nitrify for 13 months, and then succeeded only after re-seeding with soil. At that date, I was anxious to obtain nearly clear solutions in which to observe nitrification, and I therefore tried to replace the carbonate of lime by soda or potash, and to substitute some other form of organic matter for the alkaline tartrate hitherto generally employed, and supposed to serve as aliment for the nitrifying organism. When an alkaline tartrate or any similar substance is employed, a bacterial fermentation is set up almost immediately, which destroys nitrates if they happen to exist already in the liquid experimented on, and at any rate renders the whole liquid turbid from the presence of myriads of organisms. These die down after a few days and form a deposit at the bottom of the liquid, but they never leave the liquid absolutely clear. At a later stage I was able to avoid these bacteria altogether, to do without tartrates or similar substances, and to obtain almost perfectly clear nitrifying solutions, but my earliest attempts almost all failed at the first seeding, apparently because 1 or 2 mgrms. soil is insufficient to induce nitrification in *unfavourable solutions.*

B3 contained no organic matter beyond the ethylamine itself, and that in the milligram or two of added soil. The solution was made up to contain in 100 c.c. of ammonia-free distilled water—

31	mgrms.	ethylamine hydrochloride (= 5·3 mgrms. N).
20	,,	$MgSO_4$, cryst.
20	,,	Na_2HPO_4, cryst.
17·7	,,	KHO.

The alkalinity of this solution is equal to about 145 mgrms. KHO per litre (= 36·25 ammoniacal N per million), after allowing for complete saturation of the phosphoric acid. The solution about half filled a 6-oz. stoppered reagent bottle, and was seeded with 1 *or* 2 *mgrms. only* of dry soil from 3 or 4 inches depth. It remained quite clear (except for a few flocks of magnesium phosphate) until February 2, 1884, and contained no ammonia, nitrite, or nitrate on that date. On April 7, 1884, it was still clear, but a little ammonia was present, and on August 21, 1884, more than a year after seeding, although ammonia was still present, no nitrate or nitrite could be detected, even with diphenylamine. Some time before this, viz., on November 10, 1883, thinking that the failure to nitrify might be due to the exclusion of the alkaline tartrate, I had divided this solution (together with others which had been made without tartrate, and had refused to nitrify) into two portions, one of which I placed in an open wide-mouthed bottle, with a paper cap. To this part of the solution I added a small crystal of Rochelle salt, and the bottle was

kept in a cupboard in a warm room all the winter. Yet although a delicate cloudlike fungus gradually grew in the solution, no nitrite or nitrate had developed by April 7, 1884; the solution at this date having almost dried up, was thrown away. I may mention here that in no instance did the addition of Rochelle salt to the solutions which had refused to nitrify, produce the slightest formation of nitrite or nitrate, although in every case it was speedily followed by various growths of mould. Having thus come to the conclusion that absence of the alkaline tartrate was not the reason of non-nitrification in the portion of solution which had been kept in the stoppered bottle until August 21, 1884, I on that date re-seeded it with a few more milligrams soil, and on November 13, 1884, I had the satisfaction of finding it in full nitrification, both nitrite and ammonia being present in considerable quantity. This solution was unfavourable for nitrification, since it contained a caustic alkali, but the insufficient quantity of soil added at first was evidently *the* prohibitive circumstance. It remained free from mould throughout, and is at present nearly clear. The nitrite present on November 13, 1884, has since been converted into nitrate, but ammonia is still present (March, 1886). The original alkalinity of the solution, in fact (= 14·5 mgrms. KHO), is insufficient to allow of complete nitrification, since the hydrochloric and nitric acids produced from 31 mgrms. ethylamine hydrochloride require 42·4 mgrms. KHO for saturation.

A plain solution of ethylamine hydrochloride in distilled water, containing 3 grams per litre, has remained perfectly free from ammonia and nitrite from July 20, 1883, until now (March, 1886).

II. *Nitrification of Potassium Thiocyanate.*

The thiocyanates, it is well known, are poisonous to plants, and it occurred to me that possibly nitrogen in this form is not susceptible of fermentation into nitrate. I therefore included potassium thiocyanate in my first series of solutions, made on March 9, 1883. Solution (C1) contained 243 mgrms. KCNS; 222 mgrms. potassium bitartrate; 222 mgrms. $MgSO_4$ cryst.; and 222 mgrms. Na_2HPO_4 cryst., in 500 c.c. ammonia-free distilled water. Calcium carbonate and 2 grams moist soil were added. Total N = 35 mgrms. Until March 26 no change occurred. Ammonia then slowly developed, and a mould began to grow. On July 19, 33 mgrms. N existed as ammonia, and a trace of nitrite was present. On August 16 the ammonia had fallen to 12 mgrms. N, and the nitrite had increased; as the thiocyanate itself decolorises permanganate, no estimation was possible. A little nitrite was still present on October 18, although there was then no ammonia. On October 29, both nitrite

and ammonia were absent, and the N as nitrate was estimated at 27 mgrms., a nitrification of nearly 80 per cent. As showing the complete oxidation of the thiocyanate, I may mention that when made up, and even on March 26, 5 c.c. of the solution decolorised 14·4 c.c. of standard permanganate; on October 29, one drop of permanganate sufficed to colour the liquid. The reaction with ferric salts disappeared before June 9.

It appears from this experiment that thiocyanates are easily nitrified by soil, and that as in other cases, ammonia, nitrite, and nitrate appear in succession. A plain dilute solution of potassium thiocyanate in distilled water, made up March 9, 1883, is now, three years later, quite free from nitrite and nitrate. It has grown a few spots of mould, however, and contains a trace of ammonia.

III. *Nitrification of Ammonium Thiocyanate. Experiment with Thiocarbamide.*

Although ammonium thiocyanate is a plant poison, its isomeride, thiocarbamide, is stated by Dr. Emerson Reynolds to act as a nitrogenous manure. It is curious that in the following experiments I should have succeeded in nitrifying the former, whilst the latter has resisted nitrification for nearly three years. The ammonium thiocyanate resisted nitrification for 13 months, because of the sterility of the 1 or 2 mgrms. of soil with which the solution was seeded, but it commenced to nitrify very shortly after being re-seeded with soil; re-seeding, however, has *not* induced nitrification of the thiocarbamide.

Ammonium Thiocyanate.—Solution G1, made up July 20, 1883. The 100 c.c. ammonia-free distilled water contained 35 mgrms. NH_4CNS; 20 mgrms. $MgSO_4$ cryst.; 20 mgrms. Na_2HPO_4 cryst., and 20 mgrms. oxalic acid crystals neutralised by addition of 17·7 mgrms. KHO. 1 or 2 mgrms. dry soil were added, and a little magnesium carbonate. This bottle, it will be seen, belongs to the first series, from which I excluded tartrates, on account of their liability to encourage reducing bacteria and moulds. Organic carbon was supplied in the form of an oxalate, and this made no difference to the eventual nitrification of the solution, although I for some time believed that it would. I now believe that the oxalate might also have been omitted, but prefer to discuss the influence of organic matter on nitrification in the light of subsequent experiments.

Progress of the solution:—Up to November 10, 1883, no change could be detected, the solution giving the reactions for oxalates, ammonia, and thiocyanates, remaining perfectly clear, and giving no evidence of nitrite or nitrate with metaphenylenediamine or

indigo. Half of the solution was then removed to a shallow bottle, a crystal of Rochelle salt added, and the bottle placed in a warm cupboard for the winter. On February 2, 1884, it began to grow a mould, which increased in amount until April 7, 1884, when the solution was thrown away, having completely failed to nitrify, notwithstanding the addition of tartrate. The half solution containing no tartrate was kept in its stoppered bottle until August 14, 1884, and as it showed no nitrification or other apparent change at this date, 13 months after being made up, it was re-seeded with a few milligrams of soil. By November 13, 1884, abundance of nitrite was formed, but ammonia was still present. Since then, both ammonia and nitrite have been converted into nitrate, and the reaction with ferric salts has disappeared. The addition of a sufficient quantity of soil was therefore the indispensable condition of nitrification with this solution.

Thiocarbamide.—I prepared this substance in the ordinary manner by heating ammonium thiocyanate at 170° C. for some time, but I could not free it entirely from traces of that salt. The solution for nitrification was of the same strength, and was made up on the same date (July 20, 1883) as the corresponding one of ammonium thiocyanate, and it was in all respects similarly treated. I need therefore only say that it entirely failed to nitrify, even after re-seeding with soil, and on March 13, 1886, it contained neither nitrite nor nitrate. The reaction with ferric salts, due to the small admixture of thiocyanate, gradually disappeared, but the thiocarbamide appears to have suffered no change.

Quite recently I have made a third attempt to nitrify this solution. A gram of fresh soil was added three months ago, but as I write (June 8, 1886) the solution is unaltered, and there is no sign of nitrification. After three seedings, and a period of trial extending over nearly three years, we may conclude with tolerable certainty that thiocarbamide is not nitrifiable; very probably it exercises an antiseptic action fatal to nitrification, for otherwise the traces of ammonium thiocyanate with which it was contaminated would certainly have furnished nitrate sufficient for detection.

Plain solutions of ammonium thiocyanate and of thiocarbamide in distilled water (1 mgrm. per c.c.) have remained free from nitrite or nitrate, and without apparent alteration, for nearly three years.

IV. *Nitrification of Urea.*

Diluted urine has been used as a medium for nitrification in many of Mr. Warington's experiments, and in the summer of 1883 I made up a few solutions from instructions which he was kind enough to

give me. I need only say that they nitrified quickly, passing through the usual stages of ammonia, nitrite, nitrate. The two experiments now to be described were made with pure crystallised urea, in order to see whether nitrification would take place without the presence of the organic matter which accompanies urea in urine. To the first bottle (F1) I therefore added organic carbon in the shape of an oxalate only; the solution eventually nitrified (and I believe would have done so without the oxalate). The second bottle (F2) was like the first, but soil was entirely omitted. The behaviour of these two solutions exhibits very well the vital relation of soil to the process of nitrification. F1 seeded at first with only a milligram or two of soil, refused to nitrify for 13 months, when re-seeding with a few milligrams of soil speedily set up nitrification. F2, although not sterilised by heat, has remained for 2 years and 8 months without showing a sign of nitrification. It developed ammonia, though more slowly than F1; but in the absence of soil the ammonia showed no tendency to pass into nitrite or nitrate, notwithstanding the supply of salifiable base at hand. All the experiments have tended to convince me that the ammoniacal ferment is far more generally diffused than the nitric ferment.

The solutions were made up July 20, 1883. Total N in each = 9·3 mgrms.

F1. 100 c.c. contained 20 mgrms. urea; 20 mgrms. $MgSO_4$ cryst.; 20 mgrms. Na_2HPO_4 cryst.; and 20 mgrms. crystallised oxalic acid neutralised with 17·7 mgams. KHO. A little magnesium carbonate and 1 or 2 mgrms. soil were added.

F2. Exactly like F1, but with no soil.

Aug. 1, 1883. F1 contains 0·2 mgrm. NH_3. F2 contains no NH_3.
Aug. 16, 1883. F1 contains 0·4 mgrm. NH_3. F2 ,, ,,
Aug. 21, 1883. F1 contains 0·7 mgrm. NH_3. F2 ,, ,,
Oct. 18, 1883. F2 contains trace NH_3.
Nov. 10, 1883. F1 contains 1·0 mgrm. NH_3. F2 contains 2·5 mgrms. NH_3.

When once contaminated, therefore, F2 developed ammonia faster than F1. No nitrite or nitrate having appeared in either solution to this date, half of each solution was removed to another bottle, and a crystal of Rochelle salt added as explained in previous sections. These tartrated solutions remained without nitrification (although the one with soil eventually grew a mould) until April, 7, 1884, when they were thrown away.

Aug. 14, 1884. F1 and F2 (not tartrated) are clear, free from mould, contain ammonia but no nitrite or

nitrate. F1 was now re-seeded with a few milligrams of soil.

Nov. 13, 1884. F1 contains ammonia and nitrite, and is therefore nitrifying.

F2 contains ammonia but no nitrite or nitrate.

Mar. 13, 1886. F1 contains a trace of ammonia and much nitrite. $MgCO_3$ still in excess.

F2 contains much ammonia, no nitrite or nitrate.

The nitrification of F1 is, therefore, even now not complete, and is chiefly, perhaps wholly, nitrous. The quantity of liquid remaining is too small for analysis.

After the last testing, March 13, 1886, E2 was seeded with soil, and it is now, June 10, 1886, in full nitrification.

A plain solution of urea in distilled water (5 mgrms. per c.c.) behaved like F2. Soon after being made up (July 20, 1883), it developed a little ammonia, which it still contains, but no nitrite or nitrate. Most ammonia-forming substances, when dissolved in distilled water, give rise to *a little* ammonia, unless the solutions are sterilised by heat and protected from the entrance of ordinary air. The ammonia-forming ferment, however, does not cause nitrification even in presence of supply of base.

V. *Nitrification of Gelatin.*

The sample of gelatin used contained 19·0 per cent. of water. 250 mgrms. were dissolved in 500 c.c. water and 222 mgrms. each of crystallised magnesium sulphate, sodium phosphate, and potassium bitartrate, added to the solution. Carbonate of lime and 2 grams moist soil were also added. The solution belonged to the first series and was treated in all respects like its companions.

Mar. 9, 1883. Made up. Total nitrogen present = 36 mgrms.

Mar. 15, 1883. No ammonia.

Mar. 26, 1883. Ammonia = 4 mgrms. nitrogen. The solution turbid, tufts of mycelium on surface.

April 1, 1883. Ammonia = 12 mgrms. nitrogen. Turbidity and flocks of mycelium much increased, odour putrid.

April 13, 1883. Ammonia = 29 mgrms. nitrogen. No odour; turbidity lessened; shows dead bacteria under microscope. No nitrite or nitrate.

June 4, 1883. NH_3 present. No nitrite or nitrate.

July 9, 1883. NH_3 absent. The solution decolorises indigo. Nitrite present.

July 23, 1883. No ammonia or nitrate. 32 mgrms. nitrogen present as nitrate.

This experiment exhibits the ordinary course of nitrification of nitrogenous organic matter under favourable circumstances. First came a putrid bacterial fermentation, during which nearly all the nitrogen was transformed into ammonia. This was succeeded by a pause until the weather became warm enough for nitrification, which set in some time between June 4 and July 9, and progressed very rapidly. Nitrite was at first found, but speedily disappeared, and on July 23, 88 per cent. of the nitrogen of the gelatine existed as nitrate.

A plain solution of gelatin was also made up March 9, 1883, in boiling distilled water in a long-necked stoppered flask. The stopper was removed occasionally when tests were made, so that slight contamination from the air was quite possible. In a few days the solution began to grow turbid, developed a putrid odour, and gave a green colour with Nessler solution. After a little while, the ordinary ammonia colour was given with Nessler reagent, but the production of ammonia soon ceased. The turbidity decreased, and the solution remained without further change until August 21, 1884, on which date it was nearly clear, but still contained ammonia and retained the putrid odour. No nitrite or nitrate was present, and in order to see whether the addition of a salifiable base would produce nitrification a little magnesium carbonate was put in. The solution still (March 13, 1886) contains ammonia, but no nitrite or nitrate, thus supporting the soil-ferment theory of nitrification.

VI. *Nitrification of Urine.*

Four experiments with diluted urine, I record here because they present two instances of nitrification through accidental fertilisation of the solutions. The peculiar behaviour of these solutions, far from being opposed to the ferment theory of nitrification, is quite in harmony with it.

E1 and E2 were made up June 11, 1883. 500 c.c. ammonia-free water with 2 c.c. urine were placed in two litre flasks, which were plunged in boiling water for 30 minutes; the necks of the flasks were plugged with cotton-wool while steam was issuing. When cold, a little unsterilised calcium carbonate, in fine powder, was added to each. E1 was seeded with soil. E2 was not seeded. Both flasks were covered with paper caps, and kept in the dark.

In 28 days E1 contained 20—24 mgrms. N as ammonia, and nitrification had commenced.

In 50 days 17 mgrms. N were present as nitrite, and oxidation to nitrate was completed during the next month.

E2, on the contrary, although it developed ammonia nearly as fast as E1, showed no sign of nitrification in 50 days. But after 113 days,

20 mgrms. N were present as nitrite, which took more than two months longer to pass into nitrate. There are three possible sources of contamination in this experiment; the unsterilised calcium carbonate, the entrance of air and dust during the 7 or 8 removals of the cotton-wool plug for testing purposes, and the use of pipettes for testing which were washed simply with distilled water instead of boiling water. The next pair of experiments fixes the responsibility upon the last circumstance, since the two former possible sources of contamination were present without causing nitrification, but when the third source was introduced, nitrification followed.

E3 and E4, made up November 10, 1883. Each consisted of 1 c.c. urine in 100 c.c. water, with a little calcium carbonate. The liquids were not sterilised by heat, and were placed in stoppered bottles, half full. E3 was seeded with five drops of the accidentally contaminated solution E2. E4 was not seeded.

E3 showed signs of nitrification in 37 days, and the nitrite present gradually increased until on the 155th day it amounted to 12 mgrms. N, which passed into nitrate before the next testing made on the 225th day.

The stopper of E4 *was not removed during the first* 155 *days*, at the end of which time neither nitrite nor nitrate could be detected. The stopper was replaced and *not removed again until the 225th day*, when there was still no sign of nitrification. At the third removal of the stopper, however, on the 283rd day, 8 mgrms. N were found as nitrite, which had not increased at the fourth testing made on the 368th day. Up to this time, therefore, the very slight accidental contamination had caused a very slow, incomplete, and purely nitrous fermentation. The addition of *a centigram of soil* on this date, caused rapid and complete conversion into nitrate.

VII. *Nitrification of Ammonium Salts in Artificial Solutions.*

The first solutions made up included strong and weak solutions of ammonium chloride, an intermediate solution of ammonium chloride not fertilised by soil nor sterilised by heat, and a solution of ammonium oxalate.

Strong and Weak Solutions of Ammonium Chloride.

The weak solution (A1) contained 400 mgrms. of the salt per litre; the strong solution (A2) 2000 mgrms. per litre. Mr. Warington's weak solutions contain generally 80 mgrms. NH_4Cl per litre, and when his second report was published (1879), the strongest solution nitrified contained 640 mgrms. per litre. He states in his last report (December, 1884) that he has since completely nitrified

solutions containing 1280 mgrms. per litre, and that solutions containing as much as 8000 mgrms. are in process of nitrification. My solutions were made up on March 9, 1883; to 500 c.c. of each were added 222 mgrms. potassium bitartrate; 222 mgrms. $MgSO_4$ cryst.; 222 mgrms. Na_2HSO_4 cryst.; a teaspoonful of calcium carbonate; and 2 grams of moist soil. The progress of the solutions (kept in stoppered bottles, half-full, in a cupboard at the ordinary temperature of the laboratory) is shown in the following table:—

March 9, 1883. Made up. A1 contained 52·3 mgrms. N, and A2 contained 262 mgrms. N. Tested and Nesslerised at intervals, neither of them showed diminution in ammonia, or presence of nitrite or nitrate up to June 4, 1883. Between this date and July 9, 1883, both began to nitrify. The subsequent course of the weaker solution A1 was as follows:—

July 9, 1883. Ammonia = 33 mgrms. N. Decolorises indigo.
" 23, 1883. No nitrite. Nitrate = 23 mgrms. N.
Aug. 16, 1883. Ammonia = 15 mgrms. N. Nitrite = 9 mgrms. N.
Nitrate = 28 mgrms. N. (by diff.).
Oct. 18, 1883. No ammonia. No nitrite. Nitrate = $47\frac{1}{2}$ mgrms. N.

Nitrite was doubtless present between June 4 and July 23, but it was not tested for; at any rate it had been entirely converted into nitrate by the latter date, between which and August 16 a fresh formation of nitrite took place, and the solution was completely nitrified into nitrate during the long vacation.

The progress of the strong solution (A2), only a third of whose nitrogen was oxidised to nitrite when A1 had run its complete course, is shown by the estimations of nitrite made at the following dates:—

July 9, 1883.	Nitrite present.	
" 23, 1883.	Nitrite = 70 mgrms. N.	
Aug. 16, 1883.	" = 88 " N.	Ammonia estimated at 165 mgrms. N.
Oct. 18, 1883.	" = 87 " N.	Ammonia estimated at 144 mgrms. N.
Feb. 7, 1884.	Nitrite = 86 mgrms. N.	
" 27, 1884.	" = 86 " N.	
Apr. 7, 1884.	" = 35 " N.	Nitrite and nitrate estimated at 115 mgrms. N.
June 24, 1884.	" = 35 " N.	
Aug. 19, 1884.	" = 175 " N.	No ammonia.
Nov. 11, 1884.	" = 175 " N.	
Mar. 18, 1886.	" = 86 " N.	Nitrite and nitrate estimated at 236 mgrms. N.
June 5, 1886.	" None.	

The completion of nitrification in this solution has only taken place since I commenced preparing this paper for publication, and altogether the process has occupied *more than two years and nine months.* But the solution and residue remaining in the bottle now contain so much of the nitrifying ferment that 250 c.c. of strong ammonium chloride solution (1 gram per litre), added bodily, has commenced to nitrify in *five* days.

Unfertilised Solutions of Ammonium Chloride, sterilised by Heat, and not sterilised.

A solution (A3*b*—March 9, 1883) of ammonium chloride like A1, but with the soil omitted, underwent a tardy and for a time entirely nitrous fermentation; a second solution (A4*b*) made up November 10, 1883, also unseeded, nitrified completely to nitrite after some time, and the nitrite has persisted ever since. Both of these solutions were unsterilised by heat and were kept in ordinary stoppered bottles, half-full. The nitrification of A4*b* was much slower than that of a similar solution (A5) made up at the same time, and seeded with five drops only of a nitrifying solution (A2), although both nitrified to nitrite only. I have succeeded in ascertaining definitely that the standard ammonium chloride* employed in making up A3*b* and A4*b* was itself contaminated with a trace of the nitrous ferment; it had been made up two years before, and *all* the solutions in which it was used *which were not sterilised*, eventually nitrified. On the other hand, two *boiled* solutions (AB1, AB2) in flasks with cotton-wool plugs and paper caps, which were made up as checks on April 14, 1884, and not opened until March 18, 1886, have remained without the formation of any nitrate or nitrite; they still contain plenty of ammonia.

Nitrification of Ammonium Oxalate.

A solution of the first series (A9, March 9, 1883) contained 250 mgrms. of the crystallised salt. It nitrified to nitrate even more rapidly than the corresponding solution of ammonium chloride made up on the same day. I have since ascertained (p. 648) that the oxalic acid is destroyed long before nitrification sets in. By taking advantage of this fact, ammonium oxalate can be completely nitrified with half the proportion of salifiable base necessary when ammonium chloride is used, and sodium or potassium oxalate may be used in place of the salifiable base usually employed.

* See note, p. 654.

Nitrification of Ammonium Chloride; Organic Carbon added in the form of Potassium Oxalate only.

On July 20, 1883, nine solutions were made up without an alkaline tartrate; in eight of these, potassium oxalate was substituted; the ninth, in which ethylamine was to be nitrified instead of ammonia, contained neither tartrate nor oxalate. The history of five of the solutions, containing respectively ethylamine, ammonium thiocyanate, thiocarbamide, urea, and urea (not seeded), has already been given. The remaining four were devoted to ammonium chloride.

Each of these four solutions contained in 100 c.c. ammonia-free distilled water—

63	mgrms.	ammonium chloride = 16·5 mgrms. N.
20	„	$MgSO_4$ cryst.
20	„	Na_2HSO_4 cryst.
26·3	„	potassium oxalate ($K_2C_2O_4$).

Three of them, A11, A12*b*, and A13*c*, were rendered alkaline by magnesium carbonate, and

A11 was fertilised with 1 or 2 mgrms. soil;

A12*b* was not fertilised;

A13*c* received 1 or 2 mgrms. soil and a few drops of chloroform.

The remaining solution,

A10, was rendered alkaline by 17·7 mgrms. KHO instead of the magnesium carbonate; it was fertilised with 1 or 2 mgrms. soil.

The four solutions were kept in 6-oz. stoppered reagent bottles in a cupboard in a warm room, and were examined at frequent intervals.

Three and a half months after making up, viz., on November 10, 1883, as no nitrite or nitrate had formed in any of them, half of each solution was removed to a wide-mouthed bottle, a crystal of Rochelle salt dissolved in each of these halves, and the bottles covered with loose paper caps. These tartrated halves of the solutions were examined at intervals up to April 7, 1884, when evaporation and frequent testings had reduced them to a very small bulk; they were then thrown away. On that date, nearly eight months after being made up, and five months after addition of tartrate, neither of them had commenced to nitrify. A13*c*, from which the chloroform had of course disappeared long before, had grown a patch of mould, but the other three were quite free from mould.

The untartrated halves of the solutions, in the stoppered bottles, were also free from moulds and from nitrite or nitrate on April 7, 1884, and they were not again examined until August 21, 1884, 13 months after being made up. On this date, one only of the four had undergone partial nitrification; this was A11, which had always been con-

sidered the most favourable solution, since it contained magnesium carbonate instead of caustic potash, and was seeded with soil. The $MgCO_3$ deposit had all disappeared, and the stopper jumped out when loosened, from accumulation of carbon dioxide gas. Ammonia was still present, but the reaction of the liquid, originally alkaline, was now faintly acid. 10 mgrms. nitrogen were present as nitrite, so that nitrification had evidently proceeded until all the available base was saturated. Some more $MgCO_3$ was added at this date, and the solution again examined on November 13, 1884, when all the ammonia had disappeared, and $14\frac{1}{2}$ mgrms. nitrogen were present as nitrite, out of the $16\frac{1}{2}$ mgrms. originally added as ammonia. The nitrite has persisted without alteration for another 16 months, so that the fermentation in this solution was purely nitrous throughout.

A10, the caustic potash solution, was re-seeded with a few milligrams of soil on August 14, 1884, and by November 13, 1884, this also had nitrified entirely to nitrite, and the nitrite still persists without diminution (March 19, 1886).

To A12*b*, the unseeded solution, a little fresh $MgCO_3$ was added on August 21, 1884, but up to the present date no nitrification whatever has taken place, and the solution gives a deep brown precipitate with Nessler's test. Here we have another instance of a non-fertilised but also non-sterilised solution, refusing to nitrify for two years and four months, although exposed to occasional chances of contamination from the air.

To A13*c*, the fertilised but chloroformed solution, some more soil was added August 21, 1884. On November 13, 1884, the odour of chloroform was very faint, but no nitrification had occurred. To-day (March 19, 1886) there is no odour of chloroform, but still there is no nitrification, and the solution gives an abundant brown precipitate with Nessler test. Of these four solutions then—

A11, with $MgCO_3$ as base, underwent a complete nitrous fermentation without re-seeding, but after a long delay.

A10, with KHO as base, underwent a complete nitrous fermentation, but only after re-seeding.

A12*b*, with $MgCO_3$ as base, but not fertilised, has altogether refused to nitrify.

A13*c*, with $MgCO_3$ as base, fertilised and chloroformed, has altogether refused to nitrify, even after re-seeding.

These solutions, therefore, strongly support the ferment theory of nitrification.

As regards the substitution of an oxalate for a tartrate, it remains for me to add that in four out of the eight solutions to which it was added, the oxalate had completely disappeared one month afterwards

(August 16, 1883). Three out of these four solutions had been seeded with soil. The two solutions in which the oxalate persisted unaltered for some months, were the *unfertilised* solution A12*b* and the *chloroformed* solution A13*c*.

These facts suggested to me that the oxalate was decomposed by the agency of soil ferments, and hence that its "organic carbon" exercised no influence on the nitrification. I have recently verified this. Solutions of alkaline oxalates are rapidly attacked by soil ferments; they become opalescent with bacteria, the oxalate is destroyed in a few days, and an alkaline carbonate is found in its place. This change is entirely prevented by boiling, and to a great extent by chloroform. It follows from this that an alkaline oxalate may be used as *salifiable base* in nitrification experiments. For example, 100 mgrms. ammonium oxalate crystals were completely nitrified with 170 mgrms. sodium oxalate as salifiable base. The oxalate was entirely destroyed by the 5th day; nitrification commenced between the 21st and 26th day; three-fourths of the nitrogen was present as nitrite on the 65th day, and nitrification to nitrate was finished before the 80th day.

Nitrification in boiled, filtered, transparent solutions of Ammonium Chloride.

Three solutions were made up on November 10, 1883, with the especial object of studying the influence of nitrification on the transparency of a solution and of observing the formation or non-formation of a deposit or surface growth. Sodium bicarbonate was, therefore, used as the salifiable base instead of calcium or magnesium carbonates; the solution was filtered twice through Swedish paper, boiled, and protected from the entrance of unfiltered air; and fertilisation was effected in one case by only 1 or 2 mgrms. soil, and in the other case by five drops of an apparently clear solution undergoing the nitrous fermentation (A2). The third solution was not fertilised and was not opened for six months after making up. Each solution contained in 100 c.c. ammonia-free distilled water—

63	mgrms.	NH_4Cl = 16·5 mgrms. N.
40	,,	Rochelle salt cryst.
10	,,	$MgSO_4$ cryst.
10	,,	Na_2HPO_4 cryst.
60	,,	$NaHCO_3$.

These solutions were filtered through double Swedish filters into narrow-necked 200 c.c. flasks, previously cleansed with boiling pure sulphuric acid. The solutions were sterilised by boiling, the necks of

the flasks were plugged with cotton-wool while steam was issuing, and, on cooling, paper caps were tied over the mouths. Of course some ammonia was lost during the boiling, and also subsequently by evaporation through the cotton-wool plugs, but plenty remained intact and underwent nitrification in due course.

The flasks were locked in a bureau in a living room, and were examined as to transparency, &c., from time to time. The cotton-wool plugs of two of them, A6 and A7, were removed on the cooling of the solutions for the introduction of the ferment, and at intervals afterwards in order to mark by testing the commencement of nitrification; the plug and cap of A8*b*, the unfertilised solution, remained untouched from November 10, 1883, to April 14, 1884. The following observations were made at the dates specified:—

Nov. 20, 1883. The solutions A6 (fertilised with a mgrm. of soil) and A7 (fertilised with five drops of a nitrifying solution) are both opalescent. There is no sign of nitrification. The opalescence of A6 is seen under the microscope ($\frac{1}{10}''$ objective) to be caused by bacteria, which exhibit a slow oscillating motion, a few rotifers are also present in active motion.

Dec. 3, 1883. A6 has become clearer; A7 still turbid.

Dec. 9, 1883. A6 still clearer; dead bacteria are settling down in minute patches. A7 still turbid. No nitrification in either.

Jan. 24, 1884. A6 clear, with deposit of dead bacteria. Nitrification has commenced.

A7 nearly clear, with deposit of dead bacteria; three or four tufts of mould have commenced to grow from the bottom. Nitrification has commenced.

Feb. 15, 1884. A6, appearance unaltered. Contains nitrite.

A7 not quite clear. Clouds of mould increased. Contains nitrite.

April 9, 1884. A6 still contains ammonia. Nitrogen as nitrite = $1\frac{1}{2}$ mgrm. Nitrate also present, but no exact estimation could be made.

A7 still contains ammonia. Nitrogen as nitrite = 2 mgrms. Doubtful whether any nitrate present.

Up to this date, therefore, A6 had undergone a partial fermentation into nitrite and nitrate, and A7 a partial fermentation into nitrite. The unfertilised solution A8*b*, opened for the first time April 14, 1884, was *absolutely* bright and clear, and contained not a trace of nitrite or nitrate. Compared with this solution, the clearness

of A6 and A7 was seen to be far from perfect; A6 was the clearer o. the two, but was faintly opalescent.

June 24, 1884. A6 and A7 still contained ammonia; nitrite diminished to $\frac{1}{2}$ to $1\frac{1}{4}$ mgrm. N respectively.

The unfertilised solution A8*b* did not remain absolutely bright after being opened on April 9. It soon developed a delicate opalescence, which remained on June 24, 1884. There was then no sign of nitrification, however, so that the first temporary exposure to the air, although it had certainly introduced germs into the solution, had not inoculated it with the nitrifying ferment.

Aug. 21, 1884. By this time A8*b* had begun to nitrify, so that the second exposure or testing on June 24 was fatal to it. Ammonia was still present. The N as nitrite was 2·8 mgrms., and a very careful estimation (after oxidation with permanganate) of the total N as nitrate gave 2·77 mgrms. Evidently, therefore, the fermentation was *purely* nitrous. The opalescence previously noticed had ended in a slight flocculent deposit.

A6. The nitrite has now disappeared, but ammonia is still present.

A7. The nitrite has increased to 5 mgrms. N, but ammonia is still present.

Nitrification in A6 and A7 being arrested by saturation of the sodium bicarbonate, more of this salt was added to each solution on this date. By November 13, 1884, A6 had nitrified completely to nitrate; A7 afterwards nitrified completely to *nitrite;* in A8*b*, the formation of nitrite has proceeded more slowly, and even now a little ammonia is unnitrified.

Of these solutions, therefore, the only one that has, in 32 months, completely nitrified to nitrate is the one seeded with soil; the solution seeded with a nitrous fermenting solution, has nitrified completely to nitrite; and the unseeded solution, which remained absolutely intact so long as it was not exposed to contamination, has partially nitrified to nitrite. These results are in exact accordance with Mr. Warington's conclusions, and are scarcely explicable by any other theory than that of ferment introduced from without.

The difficulty in producing nitrification in otherwise clear tartrated solutions will be seen from the above description to be very great. The organisms which render so many organic infusions opalescent after even a momentary exposure to unfiltered air, are immensely more abundant than the nitric ferment, and very much easier of cultivation; and they not only attack the organic matter and render the solutions turbid, but they reduce and sometimes destroy any nitrate that may be present in the liquid. Unless ordinary bacterial germs are rigorously excluded, therefore, the presence of organic matter of this sort must be prejudicial to nitrification.

This exclusion may possibly be accomplished by employing a very pure cultivation of the nitrifying organism, and by permitting the access of filtered air only. But a much easier method of avoiding the multiplication of these bacteria is to exclude Rochelle salt or any similar organic matter from the solutions; and this may be done either by relying on the organic carbon in the soil used for seeding, or by using, as a nitrifying medium, well water to which ammonia has been added. *The organic matter of soil and of well water, being the residue of bacterial fermentations, is impervious to the attack of the bacteria in question, and does not encourage their multiplication.* Hence such solutions remain clear, although seeded with soil and exposed to unfiltered air.

VIII. *Is Organic Carbon essential to Nitrification?*

This is a vital question, for could it be positively shown that nitrification will take place in the absolute absence of organic carbon, either the theory of an organised nitrifying ferment would fall to the ground or we should have to admit two processes of nitrification, one depending on, and the other independent of, a nitrifying organism. There is no point, however, in the whole study which is surrounded with more difficulties than this one. For granting that we succeed in excluding accidental organic matter from the distilled water, the ammonium chloride, the salifiable base, and the other minerals employed, we have still to deal with the air, perhaps filtered through a cotton-wool plug, which in itself may be a source of contamination. Even supposing these difficulties overcome, there remains the organic matter introduced with the seed, which may be either a few particles of soil or a few drops of a nitrifying solution containing added organic matter.

I therefore discuss the subject more with the view of throwing light on the practical requirements of the process of nitrification as regards organic carbon than with any intention of making the presence or absence of carbon a crux of the organism theory of nitrification. This theory is susceptible of other and easier lines of proof, and to my mind is supported by overwhelming evidence.

In nearly all of Mr. Warington's published experiments, either an alkaline tartrate (in a few cases glucose) has been added to the solutions with a view of supplying carbonaceous aliment for the nitrifying organism, or else a substance has been chosen for nitrification which in itself contained an abundant supply of organic carbon (asparagine, milk, rape cake, urine, &c.). There are, however, two experiments, recorded in his 1879 paper, in which nitrification occurred in the presence of very little carbon. These solutions contained ammonium

chloride, potassium sulphate, calcium phosphate and carbonate; some organic carbon was, however, added, for they were seeded with a small fragment of mushroom mycelium, and with 1 c.c. of a shaken up liquid which had been seeded with $1\frac{1}{4}$ grams of soil and had received 50 mgrms. potassium bitartrate as well. One of these (kept in the dark) nitrified completely to nitrate in nine months; the other, in the light, nitrified partially to nitrite. These I believe are the only recorded experiments in which the proportion of organic carbon to ammoniacal nitrogen was less than 3 : 10, exclusive of the carbon in the seed, and in most of them it was much greater. In his third (1884) report, Mr. Warington says that "probably tartrate 100 per cent. of the ammonium salt is sufficient for every purpose," and that "urine apparently contains quite enough organic carbon for its own nitrification."

Amongst the experiments already described will be found—

One (B3) in which 31 mgrms. ethylamine hydrochloride were partially nitrified into nitrate after twice seeding with a few milligrams soil;

One (G1) in which 35 mgrms. ammonium thiocyanate with 20 mgrms. oxalic acid crystals were completely nitrified into nitrate after twice seeding with a few milligrams soil;

One (F1) in which 20 mgrms. urea with 20 mgrms. cryst. oxalic acid were completely nitrified to nitrate after twice seeding with a few milligrams soil;

One (A11) in which 63 mgrms. ammonium chloride with 26·3 mgrms. potassium oxalate were completely nitrified to nitrite after *once* seeding with 1 or 2 mgrms. soil;

One (A10) in which 63 mgrms. ammonium chloride with 26·3 mgrms. potassium oxalate were completely nitrified to nitrite after twice seeding with 1 or 2 mgrms. soil.

I now know that the oxalate in these experiments had nothing to do with the nitrification, since it was destroyed long before nitrification set in.

The experiments with natural waters, presently to be described, will show that the organic carbon in well water is sufficient for the nitrification of added ammonia in quantity at least equal to the saturating power of the calcium carbonate present for the nitrous or nitric acid produced. The series of experiments which now follows, however, is more to the point, and pretty clearly exhibits the practical relation of organic carbon to nitrification.

Six solutions were made up on February 9 and 14, 1884. All contained ammonium chloride equal to 40 mgrms. NH_3 per litre (33 mgrms. N). They were carefully filtered after being made up, but *were not sterilised by heat.* A14*b* measured 500 c.c., and was con-

tained in a litre flask, the neck of which was plugged with cotton-wool; the others measured 100 c.c. each, and were contained in 6-oz. stoppered reagent bottles. The following table shows the arrangement adopted :—

Feb. 9, 1884.	A18.	Complete solution, containing per litre 126 mgrms. NH_4Cl, 200 mgrms. $NaHCO_3$, minerals (40 mgrms. $MgSO_4$ cryst., and 40 mgrms. K_3PO_4) 40 mgrms. Rochelle salt; seeded with a *few* milligrams soil.
,, ,,	A17.	*Rochelle salt only omitted.*
,, ,,	A16*b*.	*Soil only omitted.*
,, ,,	A19.	*Rochelle salt only omitted;* seeded with *several grams* of soil.
,, ,,	A15*b*.	*Rochelle salt and soil omitted.*
Feb. 4, 1884	A14*b*.	*Rochelle salt, soil, minerals, and salifiable base omitted.*

Five of these solutions, including the two unseeded ones, developed nitrite or nitrate sooner or later; but they exhibited marked differences in rapidity and extent of nitrification.

A19 nitrified completely to nitrate in less than 50 days.

A17 also rapidly nitrified; half the nitrogen was present as nitrate in 30 days; a little nitrite was formed and afterwards disappeared.

A18, differing from the last only in containing Rochelle salt, nitrified more slowly. In 30 days, less NH_3 had nitrified, and the nitrite present was considerable; during the summer, it passed completely into nitrate.

A16*b*, with Rochelle salt but no soil, underwent at first a slow and entirely nitrous fermentation; 14 mgrms. of nitrogen were present as nitrite even on November 13, 1884, but some time after that date conversion into nitrate took place.

A15*b*, *with no tartrate or soil, and therefore without added organic matter of any sort*, nitrified like the last, but still less readily. 12½ mgrms. nitrogen were present as nitrite on August 17, 1884; this increased to 15½ mgrms. on November 11, 1884, and has remained without further oxidation ever since. The clearness of the solution has never been visibly impaired.

A14*b*, without minerals, organic matter, or salifiable base, was tested five times at intervals from February 4, 1884, to August 21, 1884, but developed no nitrite or nitrate. A little sodium bicarbonate was then added, and a trace of nitrite was found on November 1, 1884, *which did not increase.* Seventeen months later, although the trace of nitrite was still present, 10 c.c. of the solution would not decolorise three drops of standard permanganate or three drops of indigotin (1 c.c. = 0·035 mgrm. N).

As regards the source of contamination in the three unseeded but unsterilised solutions, A14*b*, A15*b*, A16*b*, I have lately succeeded in proving decisively that the standard solution of ammonium chloride used, *which was not boiled*, actually contained the nitrous ferment.* The source of inoculation being known, it is not a matter of surprise that fermentation in these solutions should have taken place, but the differences in their behaviour are very significant. A14*b* with *no added organic matter or minerals*, develops only a trace of nitrite, although kept for 17 months after addition of a salifiable base. On the other hand A15*b*, *with* minerals but *no added organic matter*, undergoes *a complete but purely nitrous fermentation;* and A16*b*, for the first nine months at any rate, follows precisely the same course, although tartrate was purposely added. The merest traces of organic matter, therefore, such as may be furnished accidentally by occasional exposure to the dust of the air, are sufficient for complete nitrous fermentation of the quantities of ammonia used in these experiments; but it does not appear that the process is equally independent of purposely added minerals.

A17, again, shows that the organic matter of 1 or 2 mgrms. of soil suffices for the requirement of a complete *nitric* fermentation; and the addition of tartrate to A18 was not attended with the smallest advantage.

Moreover, unless aërial bacteria can be rigidly excluded, and nitrification carried on with *pure* cultivations of the nitric ferment instead of soil, the presence of a tartrate or any similar organic body is distinctly prejudicial to nitrification. This will appear clearly from the experiments detailed in the next section.

IX. *Nitrification of Ammonium Salts in Natural Waters.*

It is a matter of common knowledge that the ammonia and nitrogenous organic matter which find their way, say in the form of sewage, into our rivers and wells, ultimately give rise to the formation of nitrates; and the proportion of "free ammonia" and "nitrogen as nitrite and nitrate" have had their place in our analytical schemes as measures of sewage pollution "present" and "past." But few investigations, however, have taken place as to the exact manner in which the transformation of ammonia into nitrite or nitrate is effected; and such as have been made have proceeded upon purely chemical lines, the rapid aëration and large surface exposure which

* This standard solution, made up more than four years ago, now *contains* a trace of nitrite sufficient to give an orange colour with metaphenylenediamine; and by adding a little of it to *sterilised* well water, I have recently been able to effect complete conversion of the ammonia into nitrite.

moving water undergoes being tacitly or openly inferred to be sufficient causes of nitrification.

As soon as I had repeated some of Mr. Warington's experiments which strongly supported the theory of a special nitrifying organism in the soil, I commenced (November, 1883) a series of experiments with the view of ascertaining whether natural waters oxidise ammonia because of their contact with soil and the ferment contained therein, or because they themselves contain this ferment which they have obtained from the soil, or (according to then current theories) simply because they offer the ammonia the means of free and thorough atmospheric contact. The experiments were continued in 1884, but (until within the last two months) no new solutions were started after April of that year, although those then in operation have been under observation ever since in order to ascertain the completion or non-completion of nitrification in some of them.

Some months after my first experiments on waters were commenced, the late Dr. Angus Smith's last Report to the Local Government Board was published, and although he mentions some facts as to denitrification which he had observed some time before, and with which I had then become familiar from my own experiments, he does not appear to regard the oxidation of ammonia in waters in any other light than a purely chemical one. In his previous Report, indeed (1882), he says: "Putrefaction and oxidation are two well-known modes of destroying organic bodies at ordinary temperatures. The second is not proved to be connected with organisms." In the last Report he says: "Animal or vegetable matter containing nitrogen produces nitrates by oxidation with and without organisms." He illustrates the latter position by quoting experiments on the oxidation of ammonia by permanganates, and by persalts of iron, and seems to regard it as the more important process, for he says that it is "an action of the oxygen without the intervention of organisms probably carried out to a great extent in nature." Whilst fully admitting that ammonia may be oxidised by the very powerful reagents named, it is much to be doubted whether a purely chemical oxidation of ammonia ever takes place in nature when organic matter decays in contact with air, water, or soil. As regards the ordinary oxidation of nitrogenous organic matter following putrefaction, Warington's experiments with rape cake, asparagine, milk, urine, &c., show that the presence of the nitrifying ferment of the soil is a *sine quâ non* of nitrification; and the experiments which follow show the same statement to be true of the ammonia contained in natural waters.

My experiments were made by adding known quantities of ammonium chloride to waters under various conditions; and it occurred to me that if waters possessed the power of readily nitrifying ammonia

added in this way, they would form very suitable media for the study of nitrification and for the culture of the nitrifying ferment, the organic matter and minerals necessary for the nutrition of the ferment, as well as the salifiable carbonate of lime, being present in such forms as not to interfere with the clearness of the liquid. A still greater advantage is that well waters have no tendency to encourage the growth of the bacteria which multiply in and render turbid most organic infusions during the first week or two of their exposure to the air. The germs of these bacteria are present in all well waters, but they do not multiply because of the absence of *suitable* organic matter. There is one drawback to the use of well water for experiments on nitrification. In most cases it already contains nitrate. In my experiments the proportion of nitrogen as nitrate was therefore very carefully determined beforehand, and the progress of the nitrification of the added ammonium salt was ascertained by—

Testing at intervals with Nessler reagent for the disappearance of the added ammonia;

Testing with metaphenylenediamine for the appearance of nitrite, and estimating the quantity in some cases by standard potassium permanganate;

Determining by means of standard indigotin (Warington's improved process) any increase over the original nitrate present,—in the presence of nitrite *and* nitrate, the nitrite was first estimated with permanganate, and the total nitrogen then present as nitrate estimated with indigo.

The merest traces (if any) of free ammonia and nitrite were present in the waters with which I worked; and even the organic nitrogen present was in altogether insignificant proportion to the ammonia salt added, and to the ammonia actually nitrified; it did not exceed $\frac{1}{100}$th part of the added ammonia.

The standard solutions employed were of the following strength:—

Potassium permanganate..	1 c.c. = 0·072 mgrm. N	as	nitrite.
Indigotin................	1 „ = 0·03847	„	nitrate.
and	1 „ = 0·055	„	„

(Diluted to $\frac{1}{2}$, $\frac{1}{4}$, &c., according to circumstances.)

Ammonium chloride, 1 c.c. = 1 mgrm. NH_3.

Experiments with River Water.

The earliest experiments showed the rapidity and ease with which relatively large quantities of ammonium chloride could be nitrified in natural waters. Three dark glass bottles were half filled with 500 c.c.,

each of water from the River Avon, which irrigates the water meadows of the whole valley, and is frequently analysed in the College of Agriculture Laboratory.*

To each bottle was added 25 c.c. standard ammonium chloride = 20·6 mgrm. N.

α......	Received no addition beyond the ammonium chloride.
β......:	A crystal of Rochelle salt.
γ......	" " and a centigram of soil.

When made up on November 21, 1883, 10 c.c. of each of these solutions decolorised 0·53 c.c. indigotin (1 c.c. = 0·055 mgrm. N), and contained, therefore 0·204 grain N per gallon as nitrate.† The bottles were simply corked, and were kept in the dark in a bureau by the side of a fire-place in a living room.

β and γ clouded in a few days; α remained clear.

Tested on December 17, 1883, 26 days after making up, 10 c.c. α decolorised 7·4 c.c. indigotin. A little ammonia was present, but no nitrite.

Nitrogen originally present as nitrate	= 0·204	grain	per gallon.
" in added ammonia........	= 2·747	"	"
	2·951		
" as nitrate on Dec. 17, 1883	= 2·849		

2·6 grains of nitrogen in NH_4Cl require for nitrification 18·5 grains per gallon of calcium carbonate, whereas the water contained only 15 grains; doubtless the magnesia, potash, and traces of other bases in the water supplied a grain or two more of salifiable base.

* Analyses made at various times show the composition of this water to be as under:—

Total solid matter varies from	19·98	to	21·32	grains	per gallon.
Free ammonia "	0	"	trace.		
"Albuminoïd" ammonia varies from..............	0·02	"	0·08	part	per million.
Nitrogen as nitrate varies from	0·09	"	0·46	grain	per gallon.
" nitrite "	0	"	trace.		
CO_2 "	6·4	"	12·3	grains	"
Calcium carbonate "	14·58	"	15·26	"	"
Loss on ignition "	2·50	"	3·85	"	"
Chlorine "	0·92	"	1·05	"	"
Calcium sulphate "	0	"	trace.		

† It will be understood that the quantities of water taken for analysis, and the dilution of the indigotin, were varied as is necessary in working the process; but for the sake of uniformity all the results are calculated for 10 c.c. water and for indigotin, of which 1 c.c. = 0·055 mgrm. nitrogen, the strongest solution used.

Not only had β and γ *not* nitrified in the same time, but γ (soil and Rochelle salt) had lost every trace of the nitrate it originally contained, and β had lost the greater portion.

Both of these solutions eventually nitrified, but the addition of the Rochelle salt, which determined denitrification, brings them more appropriately under that head, to be considered by-and-bye. At this stage they showed me that I could with advantage eliminate Rochelle salt from my experiments, and rely on the organic carbon of the water only.

Experiments with Laboratory Well Water, commenced December 19, 1883.

A series of experiments was next made with the water of the Laboratory Well, an unpolluted but very shallow well sunk in alluvial gravel, and situated about 400 yards from the River Avon.

This well water contains—

Total solid matter	23·1 grains per gallon.		
Chlorine	1·0	,,	,,
Free ammonia	none.		
Nitrogen as nitrate	0·444	,,	,,
,, nitrite	none.		
CO_2	6—13	,,	,,
Sulphates	none.		
Calcium carbonate.........	15·4	,,	,,

2500 c.c. of this water were placed in a half-gallon "Winchester quart" and 100 c.c. standard ammonium chloride added (= 100 mgrms. NH_3 = 82·4 mgrms. N). The water was titrated with indigotin after this addition, when 10 c.c. decolorised 1·0 c.c. indigotin.

Nitrogen as nitrate	0·427 grain per gallon.		
Nitrogen added as ammonium chloride	2·217 grains		,,
	2·644	,,	,,

This was divided between 16 flasks and bottles, as in the following table :—

With no added Organic Matter.

L16. Unsterilised.
L4. Chloroformed.
L1. Boiled, and not opened or tested until April 14, 1884.
L3 Boiled, and then seeded with a few milligrams soil.

L14. Boiled, then seeded with five drops of nitrifying solution (A2).
L2. Boiled, then seeded with five drops unboiled well water.

With added Organic Matter.

L7. Rochelle salt only added.
L8. Cane-sugar only added.
L9. Glycerol only added.
L10. Sodium acetate only added.
L5. Rochelle salt added; boiled, and not opened or tested until April 14, 1884.
L6. Rochelle salt added; boiled, then seeded with soil.
L11. Rochelle salt and a little phenol added. Seeded with soil.
L13. Salicylic acid added; seeded with soil.
L12. Rochelle salt and a little chloroform added. Seeded with soil.

L 1, 2, 3, 5, 6, 15, the *boiled* solutions, were kept in flasks, half full, the necks of which were plugged with cotton-wool, and a paper cap tied over the mouths. The seed, if any, was added during a momentary withdrawal of the plug, after cooling.

The remaining solutions were kept in stoppered reagent bottles, half full, except L16, which formed a layer of about 2 inches depth at the bottom of a stoppered Winchester quart.

Of these 15 solutions five, viz., the two boiled and unseeded solutions, L1 and L5, the two chloroformed solutions, L4 and L12, and the solution with phenol, L11, absolutely refused to nitrify, although tested at intervals for more than two years after being made up. Filtered air had access to these waters through the cotton-wool plugs all that time.

Nitrification, to a greater or less extent, took place in three or four of the solutions containing added organic matter, but since in all these solutions partial or complete denitrification of the water was first produced, they are better considered under the section devoted to denitrification (p. 667).

The remaining four solutions, free from added organic matter, all nitrified completely to nitrite or nitrate, but at different rates.

L15, seeded with five drops of a strong solution in active nitrification, underwent almost complete oxidation to nitrate in less than two months; for on February 25, 1884, a trace only of nitrite was present, and nearly 3 grains per gallon of N existed as nitrate.

L3, seeded with a few milligrams of soil, completely nitrified to nitrate in about the same time as L15. Nitrite was present as late as February 4, 1884.

L16, the unboiled well water with ammonium chloride only added, completely nitrified to nitrite in less than 54 days, but the nitrite has

since remained without any further alteration for more than two years. The following table shows the dates of testing:—

Dec. 19, 1883,	10 c.c.	consume	1·1 c.c.	indigotin.	
Jan. 24, 1884,	10	,,	1·5	,,	Nitrite present.
Feb. 4, ,,	10	,,	2·6	,,	
,, 25, ,,	10	,,	2·6	,,	
Mar. 15, ,,	10	,,	2·6	,,	
Apr. 17, ,,	10	,,	2·6	,,	
Aug. 21, ,,	10	,,	2·6	,,	Nitrite = 1·96 grains N per gallon.

Nov. 11, 1884, nitrite undiminished.
Aug. 14, 1885, ,, ,,
Mar. 27, 1886, ,, ,, A little ammonia still present.
Nitrogen as nitrite and nitrate = 2·11 grains per gallon.

2·22 grains of added nitrogen (as NH_4Cl) require 15·8 grains per gallon $CaCO_3$ for complete nitrification, which is rather more than that contained in the water; hence a little ammonia escaped nitrification. The persistence of the nitrite for over two years is a very striking result, and points to an essential difference between the nitrifying power of this well water and that of the soil and nitrifying solution used in L3 and L15.

L2, boiled and seeded with 5—10 drops of the unboiled well water, also nitrified, but very slowly, and, as in the last case, nitrite only was produced. The formation of nitrite, instead of being complete in less than 54 days, had then made little progress and was not finished until two months later. The nitrite (1·96 grain N per gallon) has persisted for over two years.

Four more experiments were made with this well water, in order to see whether filtration would remove the nitrous ferment which it appeared to contain, and to again compare its behaviour with a soil-seeded water.

Each of the four solutions, L17, 18, 19, 20, consisted of 500 c.c. laboratory well water + 20 c.c. standard ammonium chloride (= 20 mgrms. NH_3 = 63 mgrms. NH_4Cl). They were treated as follows:—

L17 and 18 were filtered through two Swedish filters into cleansed and sterilised 1500 c.c. flasks, which were plugged with cotton-wool. But whereas L17 was opened and tested at short intervals, L18 was *not opened for 40 days after being made up.*

L19 was similar to the two preceding, but was seeded with a few milligrams soil.

L20 consisted of the *unfiltered* mixture, and was placed in a stop-

pered bottle to allow of accurate determinations of nitrite from time to time.

The subsequent course of these solutions is shown in the following table:—

Made up 1884.	Description.	Consumed by 10 c.c. of each water.			
		c.c. Indigotin.			c.c. Permanganate. August 26, 1884.
		Feb. 4 & 9	Feb. 25.	Mar. 20.	
Feb. 4..	L17. Filtered	1·4	1·7	2·9	4·0 = 1·96 grains N per gallon as nitrite.
„ 9..	L18. Filtered and unopened until March 20	1 4	—	2·9	4·0 = 1·96 grains N per gallon as nitrite.
„ 4..	L19. Filtered and seeded with soil	1·4	1·6	1·8	3·5 = 1·72 grains N per gallon as nitrite.
„ 4..	L20. Unfiltered	1·4	1·4	3·4	3·4 = 1·67 grains N per gallon as nitrite.

Nitrogen added as ammonium chloride = 2·22 grains per gallon.

L17, 18, 19, being in open flasks, were subject to evaporation. Careful estimations were made in L20 at intervals for two years, without showing the slightest further change. The latest determinations give—

Nitrogen as nitrite	1·67 grains per gallon.	
„ nitrite and nitrate....	1·96 „ „	*
„ nitrate..............	0·29 by difference.	

As there was about 0·54 grain per gallon of nitrogen as nitrate in the original water, it will be seen that the fermentation was purely nitrous.

L17 and L18 followed precisely the same course, showing that filtration did not remove the nitrous ferment, although it appears to have weakened it; the unfiltered solution had made more progress in nitrification on March 20 than the two filtered ones. The period of incubation in these solutions was under 21 days; temperature 60—70° F.

L19 presents an apparent anomaly. Although seeded with soil, it nitrified less rapidly than the rest, and to nitrite only. But all these bottles were kept in diffused daylight, and L19 slowly grew a powdery green alga, the spores of which were introduced with the soil. By the

* Ammonia is still present, because the salifiable base is exhausted.

continued growth of this alga, all the nitrite originally formed was gradually destroyed in the course of a year or so.

The experiments hitherto described show that whereas distilled water, even after the addition of a salifiable base, will not nitrify added ammonium chloride (A14*b*), well or river water fertilised with a particle of soil or a drop of nitrifying solution supplies everything necessary for the nitrification of added ammonium chloride to the full extent of the saturating power of the calcium carbonate present; and that nitrification in these waters, as in the artificial solutions used by Warington, is entirely prevented by boiling or by the addition of an antiseptic. But they further appear to show that river water itself is sufficiently contaminated with this soil ferment to produce a complete nitric fermentation of added ammonia; and that a well water, in five separate experiments, possessed sufficient nitrifying power to produce a complete nitrous fermentation. Also, that whilst this nitrifying power is perhaps weakened by filtration of the water through Swedish paper, it is not entirely removed.

Since Warington's experiments (1884 Report) prove that the nitrifying organism is confined to the *surface* soil, the question as to how far different natural waters become contaminated with the ferment is one that can only be settled by experiment. *A priori*, we should suppose that all surface waters, and all waters liable to accidental contamination with soil, must possess this ferment ; but it is possible that they do not all contain sufficient for the practical requirements of nitrification, and even that some protected deep well waters may be quite free from it. Quite recently, therefore, I have re-tested the well and river waters already alluded to, and have examined several other natural waters, under the following rigorous conditions :—

A flask, holding about 350 c.c., is carefully cleansed, and distilled water is then boiled in it, and a cotton-wool plug inserted in the neck. After a few minutes' boiling the plug is removed for a moment and the distilled water replaced by 5 c.c. standard ammonium chloride (= 5 mgrms. NH_3). The plug is again inserted, the ammonium chloride boiled, and the flask covered with a paper cap and allowed to cool. When cold it is taken to the water supply, the cap and plug carefully removed, and about 300 c.c. water placed in the flask, either directly from a pump or tap, or by means of a sterilised beaker. The plug is then replaced, the paper cap tied over the mouth, and the flask is placed in a warm place in the dark, and *not opened until a sufficient period has elapsed to allow of the commencement of nitrification.* If nitrification has commenced, nitrite will then in nearly all cases be present, and will give a yellow, orange, amber, or red colour with the metaphenylenediamine test, according to the amount. Should

complete nitrification have taken place, the ammonia will have disappeared; and should a partial but *purely nitric* fermentation have occurred, more indigo will be consumed than was the case with the original water. (In experiments with well waters unseeded with soil, I have hitherto invariably found *nitrite* present during the greater part of the nitrifying period.)

The following table exhibits the results obtained with six river and shallow well waters examined at Downton, and seven miscellaneous waters examined at Bristol. The samples altogether comprise shallow and deep well waters, pure waters, and waters with "present" and with "past" sewage contamination, the water of a "level" in a coal mining district, river water, and rain water. A summary of the composition of each water is given, and the result of the metaphenylenediamine test at the conclusion of the period allowed for incubation, and afterwards. The Bristol samples were kept at a temperature of 80—85° F., excepting the boiled or blank solution. This one belonged to a series made up May 7—20, 1886, but unfortunately they were slightly over-heated during a portion of the incubating period; the temperature rose to a few degrees over 100 F. on two or three days, and as a consequence all except one refused to nitrify.* That they were really sterilised by the heat is proved by the fact that duplicate flasks, made up as soon as the overheating was discovered, *all* began nitrifying in less than 18 days. These sterilised flasks, therefore, strengthen the evidence afforded by the boiled or blank solution. The Downton waters were incubated at the ordinary temperature, and with one exception commenced nitrification in less than 18 days; and this commenced nitrifying between the 18th and 23rd day.

The "rain water caught during a shower in a sterilised beaker" was of course added to some *boiled* well water, since of itself it did not contain the salifiable base and other impurities essential to nitrification.

The shorter of the two intervals mentioned under each water is the date of *first opening* and testing the flasks; a second testing was made after another few days in order to ascertain the relative rapidity of nitrification in the different waters. The colour with metaphenylenediamine on the first testing is no guide, since the nitrite *increases* during the first period of nitrification and *decreases* during the second, and it is necessary to know whether the nitrite is in the increasing or decreasing phase. The second testing accomplishes this. Thus with the Downton waters we have (see p. 666)—

* This one began to nitrify *before* the over-heating took place, and the nitrification has made no further progress since. A second testing, made 40 days after the first, still shows no nitrification in any of the other over-heated solutions.

Experiments on the Nitrifying Power

	Tests made		
	Grains per gallon.		
	Total solids.	Chlorine equal to sodium chloride.	Nitrogen as nitrate.
Bristol Waters. Incubated at 80—85° F.			
A1. Well 56 feet deep, in Coal-measures. End of pump tube 25 feet from surface. Water 10 feet from surface. Well imperfectly closed with iron plate, water raised by iron pump. Pure and clear	18·5	2·38	0·04
A2. *The same water boiled after addition of* NH_4Cl	"	"	"
A3. *The same water, a few drops lead acetate added*	"	"	"
A4. *The same water, accidentally overheated while incubating.*	"	"	"
B. Well at least 40 feet deep, in Coal-measures. Completely closed in and water raised by pump. Much polluted with recent sewage	68·9	16·2	0·03
C. Well about 70 feet deep, in Coal-measures. Over 50 feet to surface of water. Open, and water raised by bucket. Contains oxidised sewage	49·7	7·28	2·07
D. Water of old level driven under Kingswood Hill. Sample taken at the outflow, foot of Warmley Hill. Forms the water supply of the immediate neighbourhood	42·7	3·22	none or trace
E. Bristol Waterworks Co.'s water taken from their mains	17·5	1·4	0·03
F. Rain water from excavated and bricked cistern, raised by closed pump under cover	4·2	0·56	trace
G. Rain water, caught in a sterilised beaker during a shower. (*Added to boiled well water A.*)	—	trace	none
Downton Waters. Incubated at 55—65° F.			
H. River water; sample taken halfway across the Avon. Clear, with minute flocks suspended matter	19·8	1·5	0·20
I1. Shallow well (15 feet) in alluvial gravel. Water raised by horse gear and pumps, and delivered at the end of tinned lead pipe 300 feet long. Pure and clear	23·6	1·9	0·27
12. The same water filtered through Lipscombe's charcoal filter in common use	—	—	—
J. Laboratory well, very shallow, in alluvial gravel. Water raised by closed pump inside the laboratory. Pure and clear	21·3	1·6	0·37
K. Shallow well in alluvial gravel, completely closed in and water raised by pump. Contaminated with sewage three years ago. Since purified. Clear	29·3	2·5	0·37
L. Shallow well in alluvial gravel. Water raised by pump. Subject to constant contamination from farmyard sewage	34·2	4·90	0·76

* These unnitrified waters consumed the same amount of indigotin as at first.

of Rain, River, and Well Waters.

with original water.			Tests made after incubation.		
c.c. Indigo consumed by 10 c.c. of water.	Ammonia (colour with Nessler).	Nitrite (colour with meta-phenylene-diamine).	Interval after making up.	Nitrite (colour with meta-phenylene-diamine).	Ammonia (colour with Nessler test).
0·4	trace	none	19 days	deep amber	much NH_3 present.
,,	,,	,,	42 ,,	none*	,, ,, ,,
,,	,,	,,	42 ,,	,, *	,, ,, ,,
,,	,,	,,	42 ,,	,, *	,, ,, ,,
0·3	yellow ppt.	,,	19 ,,	yellow	NH_3 gone.
24·0	distinct trace	,,	19 ,,	pale yellow	much NH_3 present.
0·1?	faint trace	,,	19 ,,	red	,, ,, ,,
0·4	none	,,	19 ,,	yellow	,, ,, ,,
—	amber	,,	19 ,,	faint yellow	,, ,, ,,
—	trace	,,	21 ,,	none*	,, ,, ,,
0·8	faint trace	,,	18 ,,	yellow	much NH_3 present.
			29 ,,	very deep orange	much less NH_3.
1·1	none	,,	18 ,,	very faint yellow	much NH_3 present.
			29 ,,	bright orange	
—	,,	,,	18 ,,	yellow	much NH_3 present.
			29 ,,	deep orange	much less NH_3.
1·5	,,	,,	18 ,,	none*	much NH_3 present.
			23 ,,	faint yellow	
			29 ,,	light orange	
1·5	,,	,,	18 ,,	bright yellow	,, ,, ,,
			29 ,,	bright orange	little NH_3 present.
3·1	0·26 per million	,,	18 ,,	yellow	much NH_3 present.
			29 ,,	deep orange	

Indigotin used at Bristol, 1 c.c. = 0·01236 mgrm. N; at Downton 1 c.c. = 0·035 mgrm. N.

Depth of colour on 1st testing.	Depth of colour on 2nd testing.	Relative rapidity of nitrification.
1. *K, well water.*	1. H.	1. K, well water.
2. H, river water.	2. I2.	2. H, river water.
3. I2, well water filtered.	3. L.	3. I2, well water filtered.
4. L, well water.	4. *K, well water.*	4. L, well water.
5. I1, well water unfiltered.	5. I1.	5. I1, well water unfiltered.
6. J, laboratory well water.	6. J.	6. J, laboratory well water.

All except K were in the *ascending* stage of nitrite reaction at the 1st testing, and preserved the same order at the 2nd testing; K entered the *descending* stage before the 2nd testing, and hence is the most rapidly nitrifying water of the series. The Nessler test confirms this classification; tested again after 44 days, nitrification to nitrate was complete in K and H, the rest still contained varying quantities of nitrite.

The Bristol waters compare with each other as follows:—

Depth of colour on 1st testing.	Depth of colour on 2nd testing.	Order of nitrification.
1. D, *level water.*	1. E.	1. B, polluted well water.
2. A, well water.	2. A.	2. D, level water.
3. E, Bristol Waterworks.	3. C.	3. A, pure well water.
4. B, *well water.*	4. D, *level water.*	4. E, Bristol waterworks.
5. C, well water.	5. F.	5. C, well water.
6. F, rain water.	6. B, *no colour.*	6. F, rain water.

B contained neither nitrite nor ammonia when tested again on the 39th day; D contained nitrite but no ammonia; the remaining four still contained ammonia and much nitrite.

The sterilised solutions, it will be seen, have all refused to nitrify added ammonia. The rainwater caught from the clouds in a sterilised beaker is also destitute of nitrifying power.

With this one exception, all the natural waters examined possess the nitrifying power in a greater or less degree. The polluted well waters appeared to be most potent, then the surface waters, and last the pure and well protected wells. Very deep well waters may perhaps be either free altogether from the nitrifying organism, or contain it in such small quantities as to require a very lengthened period of incubation. It is curious that filtration through a charcoal filter should have increased the nitrifying power of the well water I, yet this is undoubtedly the case.

In other experiments, I found that the river water commences to

nitrify the added ammonium chloride in 7—9 days, the commencement of nitrification being marked by the presence of a trace of nitrite; enough nitrite to give a bright orange colour with metaphenylenediamine was present even on the 42nd day, but nitrification to nitrate was complete on the 46th day. Reinforced by the addition of 1 per cent. of soil, this water commenced nitrifying on the 3rd—4th day; very little nitrite was formed, which began to diminish after the 12th day; on the 30th day nitrification to nitrate was complete. With much soil and a thin layer of water no *nitrite*, or a mere trace, was formed.

The laboratory well water, on the other hand, has never commenced to nitrify before the 18th—22nd day; much nitrite is formed, and, as has been shown above, this water two years ago was unable to carry the oxidation of ammonia further than the stage of *nitrite*. If 150 c.c. of the boiled water be seeded with 5—10 drops of a weak nitrifying solution, about the same period of incubation is observed (18—22 days), so that the quantity of ferment in 150 c.c. of the unboiled water may be taken roughly as equal to that in a few drops of such a nitrifying solution. These experiments were made at the ordinary temperature and with 5 c.c. standard NH_4Cl(=5 mgrms. NH) to 150 c.c. of water.

In the purest well waters, there is a *very slight* flocculent deposit during nitrification; there is more deposit in the rapidly nitrifying waters. Nitrification in filtered well water, or in boiled well water seeded with a nitrifying solution free from fermentable organic matter, would probably furnish a deposit well suited for microscopic observation of the nitrifying organism, called by Schloesing and Müntz, *Micrococcus nitrificans*. In this country, I believe its existence has been inferred rather than made the subject of ocular demonstration.

X.—*Denitrification, and the Influence of Organic Matter on Nitrification.*

As already mentioned, the first three experimental solutions for observing nitrification in river water contained—

Nov. 21, 1883.

α ..	River water	+	ammonium chloride.		
β ..	"	+	"		and Rochelle salt.
γ ..	"	+	"		Rochelle salt, and soil.

The very great nitrifying power of ordinary river water without any addition was unsuspected by me at the time, and the additions of Rochelle salt, Rochelle salt and soil, to β and γ respectively, were made with the view of favouring the process of nitrification. Great, therefore, was my surprise on examining the waters 26 days afterwards, to find that whereas α had almost completely nitrified the

added ammonia to nitrate, β and γ had not commenced to nitrify, but on the contrary every trace of nitrate originally present in γ was destroyed, and most of that in β. α had remained practically clear throughout; β and γ had developed a slight turbidity (greatest in γ) a few days after making up. The subsequent course of these waters was as follows:—

β, which originally contained 0·204 grain per gallon as nitrate, contained about half this quantity 26 days after making up, and still less after another 34 days; in 30 days more there was a barely perceptible increase; in another month the indigo consumed had doubled, and between this testing, April 16, 1884, and August 21, 1884, complete conversion of the added ammonia into nitrate had taken place, about 2·8 grains per gallon of N being then present in that state. (Nitrite was present on April 16.) The solution has remained until now without further change.

The nitrate originally present in γ was *totally* destroyed during the first month, and there was a considerable flocculent deposit. Not until three months later was there any perceptible renitrification, but between April 16, 1884, and August 21, 1884, about 2 grains per gallon of ammonia was converted into nitrite, and this has since suffered complete conversion into nitrate.

Mr. Warington has observed in his last paper (1884) that denitrification precedes nitrification in certain cases. Under the head of "Reduction of Nitrates by Soil," he says: "I wish simply to call attention to the curious fact that when soil is added to diluted urine, or to other solutions suitable for nitrification, a destruction of the nitrates already present precedes the commencement of nitrification. This disappearance of the nitrates is completed in a few days. * * The reduction of the nitrates now in question is always accompanied by turbidity of the fluid."

No doubt this is strictly true as regards the solutions with which Mr. Warington experimented; these were made from substances like asparagine, urine, rape cake, milk, &c., or consisted of artificial solutions of ammonium salts to which an alkaline tartrate, cane-sugar, or glucose had been added. I shall, however, show that the presence of easily fermentable organic matter is a necessary condition of rapid denitrification; in the absence of this, soil has no tendency to reduce nitrates already formed, and indeed if it had it would not be easy to understand the formation and persistence of nitrates in arable fields and in drainage waters.

The addition of Rochelle salt to a recently nitrified solution sometimes causes a rapid and total fermentative destruction of the nitrate.

To test this point, I took the seven artificial solutions of my first series, which had undergone complete nitrification to nitrate, viz.:—

B1.	Ethylamine hydrochloride	nitrified to	nitrate.
B2.	,, ,,	,,	,,
C1.	Potassium thiocyanate	,,	,,
F1.	Gelatin	,,	,,
E1.	Urine	,,	,,
A9.	Ammonium oxalate	,,	,,
A1.	,, chloride	,,	,,

On December 18, 1883, all these solutions had remained for three or four months after complete nitrification without any further change; they were all in bottles or flasks about half full and closely stoppered or corked. On this date, a crystal of Rochelle salt was dropped into each bottle, and A1 (only) was heated for an hour in the steam-oven after this addition. When examined again on February 7, 1884, the nitrate had totally disappeared from all *except* A1; no nitrite was present in any case, and scarcely any ammonia except in F1, B1, and B2. They were, however, thick with a ropy growth of mould, so that the nitrogen of the nitrate or of the ammonia at first formed by its reduction, had been partly consumed in feeding these growths. C1 contained a black deposit and smelt strongly of sulphuretted hydrogen. A1, the sterilised solution, had remained perfectly clear, and the nitrate was intact at this date; but a few days after the stopper was removed for testing, turbidity of the solution set in, followed by a very active bacterial fermentation, with evolution of bubbles of gas. After 13 days, the solution was examined for nitrate and nitrite, and was perfectly free from them; ammonia was however present. Under the microscope, large, very active bacteria were easily seen with a $\frac{1}{4}''$ objective to be swarming in the liquid, singly and in chains of 2—8 or 10.*

Alternation of Nitrification and Denitrification.

F1, the gelatin solution which contained most ammonia after denitrification, was kept for further observation. On February 7, 1884, shortly after denitrification, it was thick with mycelium and had a putrid odour, but by April 7, 1884, it had become clear, the odour had disappeared, and a considerable amount of renitrification had taken place. By August 14, 1884, it contained no ammonia or nitrite, but 20 mgrms. N as nitrate, or about $\frac{2}{3}$ of the quantity nitrified the first time. Addition of a few crystals of sodium acetate on that date again brought about a rapid and total destruction of this nitrate, but by November 13, 1884, a *third* nitrification had commenced, which has since made considerable progress. How far this alternation of nitri-

* Probably the *Bacterium denitrificans, a* or *β*, of Gayon and Dupetit.

fication and denitrification could be carried, I do not know, but it is noteworthy that the available nitrogen diminishes after each reduction, most of it being evolved as nitrogen gas. This experiment well illustrates the relation of fermentable organic matter to denitrification.

As to the ferments themselves which bring about destruction of nitrates, they may exist in the soil, or the water, or may be derived from added impurity such as sewage, or even from the air. The particular ferment encouraged will depend on the fermentable organic matter employed, on the different species which gain access to the liquid, and on the quality of the liquid as a nutritive medium. Since nitrates are not only the most suitable nitrogenous food of green plants, but are also well adapted for the nourishment of many lower organisms, the presence of suitable organic matter in water is almost sure to encourage the growth of *some* organism or other which will sooner or later effect a destruction of nitrate. Thus a slowly growing mould or a green alga such as that already mentioned (p. 662), may feed on a nitrate and gradually destroy it, but this species of denitrification is easily distinguishable from that brought about by the bacterial ferments above mentioned. The former process may take weeks, months, or years to completely destroy the nitrate, which disappears only as fast as it is assimilated; the latter process is complete in a few days, is always accompanied by turbidity of the liquid, frequently by evolution of gas, and is marked by reduction of the nitrate to nitrite, ammonia, or nitrogen and nitrogen oxide.

In order to exhibit more clearly the antagonism between fermentable organic matter and nitrification, I will next put on record all those bottles of the Laboratory Well Water Series (p. 7) which received the addition of organic matter as well as of ammonium chloride.

(In all these cases, the original N as nitrate = 0·427 grain per gallon: the N added as NH_4Cl = 2·22 grains per gallon.)

L5. *Boiled after the addition of Rochelle Salt.*—Made up December 19, 1883. Tested on April 14, and again on August 21, not the slightest nitrification or denitrification had taken place. The addition of Rochelle salt to well waters causes after a time the separation of beautifully transparent and sometimes large crystals of calcium tartrate. It is plain from this experiment that organic matter such as Rochelle salt does not *per se* cause denitrification. Another water boiled after the addition of Rochelle salt and *soil* gave the same result.

L12. *Chloroformed after addition of Rochelle Salt and Soil.*—The history of this solution is identical with that of the preceding.

Chloroform absolutely prevented either nitrification or denitrification in the presence of soil ferments favourable to both processes.

L7. *Rochelle Salt added. Not boiled or filtered.*—This was contained in a stoppered bottle, half full. The indigo consumed by 10 c.c. at various dates was as follows:—

Dec. 19, 1883	1·2 c.c. (made up).	
Jan. 24, 1884	0·9 „	Nitrite present.
Feb. 25, „	0·9 „	
Apr. 1, „	1·2 „	
„ 16, „	1·6 „	
Aug. 21, 1884....	No nitrite and very little ammonia. Nitrification to nitrate as complete as possible.	

This is an example of what I find generally takes place in good waters. Addition of Rochelle salt produces an early and partial reduction of the nitrate to nitrite; if ammonia is present this is presently succeeded by complete nitrification to nitrate, nitrite being first formed.

L6. *Boiled after addition of Rochelle Salt; afterwards fertilised with Soil.*—The prejudicial effect of organic matter on nitrification is well marked in this experiment, for the commencement was very slow, and the fermentation was purely nitrous. In three months, the indigo consumed had barely increased, but a complete conversion of ammonia into nitrite afterwards took place, and the nitrite has persisted. Comparing this with L3 (the conditions being precisely similar except that one had Rochelle salt and the other had not), we see that the *soil alone* would have nitrified the ammonia to *nitrate* long before the commencement of even the *nitrous* fermentation in presence of Rochelle salt; indeed I have met with no instance in which after the addition of *soil alone* to a well water containing ammonia, the fermentation has stopped at the nitrous stage.

L11. *Rochelle Salt, Soil, and a little Phenol added.*—The presence of phenol interferes with the indigo process. Nevertheless, by means of the diphenylamine test, I have been able to ascertain that denitrification was nearly or quite completed in spite of the phenol, and that not the slightest nitrification has since taken place up to the present day. Abundance of ammonia is still present. There is nothing paradoxical about this. Phenol is fatal to many ferments, and amongst others to the nitric ferment, but there undoubtedly are bacteria and other organisms, which it is powerless in small doses to kill.

L13. *Salicylic Acid only added.*—The salicylic acid was added to

this bottle as an *antiseptic*, in order to study its influence on nitrification. The result was curious. Small dots or patches of mould soon began to grow at many points on the sides and bottom of the bottle, and in two months' time a gradual and nearly complete denitrification had occurred. However, after the destruction of all the salicylic acid by the mould (shown by cessation of the ferric chloride reaction), nitrification of the added ammonia set in and proceeded to a very considerable extent. (Salicylic acid interferes to some extent with the indigo process.)

Here we have a mould growing at the expense of a popular antiseptic and destroying it, and thus paving the way for nitrification of added ammonia.

L9. *Glycerol added.*—In this case, a very slow but finally complete destruction of the nitrate occurred, with a gradually increasing flocculent deposit. In the course of this reduction, a little nitrite was at one time produced. No nitrification of the added ammonia has taken place.

L10. *Crystallised Sodium Acetate added.*—I was a good deal surprised to find that a month after making up, this solution was totally destitute of nitrite or nitrate. Acetate of soda, in fact, brought about denitrification quicker and more completely than the tartrate, sugar, or glycerol, which were tried simultaneously under identical conditions with the same water; and up to the present date not the slightest renitrification has taken place. Sodium acetate, in fact, is easily fermentable in presence of a nitrate; it does not interfere with the indigo or permanganate processes, and hence is suitable for experiments on denitrification.

L8. *Cane-sugar added.*—Cane-sugar brought about a bacterial turbidity, during which the nitrate was reduced to nitrite, and subsequently a gradually increasing flocculent deposit with total denitrification occurred. Since then a mould has grown, but no nitrification has taken place.

I have now brought forward enough instances to show that what I may call fermentable organic matter, added to a water containing a little nitrate and also well fitted to nitrify ammonium chloride, undergoes a fermentation which seldom fails to destroy the nitrate already existing, and always retards nitrification of the added ammonia. If the solutions are kept in stoppered bottles (half full), nitrification of the ammonia *may* be prevented for an indefinite time, but if in open bottles or flasks, it does eventually take place. (I have no reason to suppose that the nitrifying ferment is destroyed during the denitrifica-

tion, unless in exceptional cases.) It may be thought that the exclusion of air from the liquid is the essential feature which determines denitrification, and at the same time retards nitrification. This is not the case, for rapid and complete destruction of nitrate will take place in flasks half full and freely open to the air in the case of polluted waters supplied with fermentable organic matter. In an experiment on this point, when sodium acetate was added to the water, the nitrate (1·1 grain N per gallon) was destroyed in 10 days. A little ammonia was formed from the nitrogenous matter of the sewage, and this nitrified during the summer.

The vigour and rapidity with which denitrification takes place after the addition of Rochelle salt, sugar, or sodium acetate to a well water, are closely connected with the condition of the water as regards contamination. I will give an extreme instance.

From the very large quantity of nitrate and (*for the district*) of chlorides contained in a certain well water, I strongly suspected the propinquity of a cesspool, sufficiently far removed, however, to allow of complete nitrification of all sewage finding its way into the well by percolation through the intervening gravelly soil. At any rate the water was condemned, and the following experiments made with it:—

1. A crystal of Rochelle salt was added to a portion contained in a stone jar half full. In a few days the nitrate was absolutely destroyed, the liquid was thick with bacteria, growths of mould rapidly followed the bacteria, not the slightest renitrification occurred for *at least eight months*, and at the end of that time (August 21, 1884) the water was *thick* with a ropy mould, had a very peculiar greyish-pink colour, and had developed an overpowering odour, exactly resembling that of sewage. Ammonia was present. During the 18 months since that date renitrification of this ammonia has taken place, and the odour has disappeared. The jar has been corked all the time.

2. As soon as I had noticed the very energetic denitrifying powers of this water, I procured, on February 20, 1884, a fresh sample, filled a 200 c.c. flask with it, added 140 mgrms. Rochelle salt, adapted a gas delivery-tube and graduated receiver to the neck of the flask, and placed it on a warm shelf in diffused daylight. The water clouded on the third day, gas began to be evolved on the fourth, increasing in amount up to the eighth, when 10 c.c. had collected. The fermentation was now practically over, the swarms of bacteria*

* I examined these bacteria with the microscope, and made a drawing of them. The recent publication of Gayon and Dupetit's memoir enables me to recognise them as *Bacterium denitrificans*, isolated by them in successive cultivations of a drop of sewage in artificial media.

died down, and the water again became comparatively clear. It gave not the slightest reaction with the diphenylamine test, but smelt *strongly of sulphuretted hydrogen*, and gave a black precipitate with lead acetate. The gas had all the characters of nitrogen.

This is the most energetic denitrification I have witnessed in a well water not containing unoxidised sewage (no free ammonia); not only was the nitrate totally destroyed, but the small quantity of sulphate was reduced to H_2S. It impressed me very much at the time, and caused me to make some experiments with a view of devising a mode of testing waters based on their power of denitrification in presence of suitable organic matter.

Shortly afterwards the late Dr. Angus Smith's last report appeared in print, and in it he proposed a method of examining waters very similar in principle. It is based on his observation that sugar, when added to certain waters, undergoes a bacterial fermentation with evolution of hydrogen gas. He had also observed, in 1881, that the addition of excreta to a solution of nitre, causes an evolution of nitrogen equivalent to the whole of the nitre employed. Gayon and Dupetit have observed that when sewage is added to chicken broth and other organic infusions to which nitre has been added, a strong denitrifying fermentation is set up, resulting in the evolution of gaseous nitrogen.

The experiment described above, and others which it is not necessary to detail, led me to recognise that sewage, soils, and most waters contain organisms which are capable of provoking denitrification, and that the one circumstance necessary to determine this action is the presence of fermentable organic matter—not sugar alone, but probably the great majority of organic compounds found in plants and animals, and including such simple substances as acetates, and even oxalates.

Dr. Angus Smith's test for the bacterial activity of a water was to add cane-sugar, and observe the activity of the fermentation produced, and the quantity of hydrogen gas evolved in a given time. He remarks on the irregularity of some of the results as regards production of gas, and this irregularity may, I think, be explained by the relation of nitrates to this fermentation. The waters examined would contain very variable quantities of nitrate, some none at all, and its presence or absence greatly influences the result. In the first place a water exempt from nitrate is very unfavourable to the fermentation, because ferments of this class are greatly encouraged by a large supply of nitric or ammoniacal food. In the second place, if nitrate is present it may be decomposed in various ways, and may either prevent the evolution of hydrogen or substitute that of nitrogen and oxides of nitrogen.

It is possible, therefore, that an improvement on Dr. Angus Smith's proposed mode of examining waters may be made by adding a little nitrate to waters deficient in it, together with appropriate organic matter, and observing the extent and kind of denitrification produced. Denitrification to a greater or less extent will always occur, whereas evolution of hydrogen is an exceptional circumstance. I have worked a little in this direction and will summarise my results.

The addition of Rochelle salt, sugar, acetate of soda, or even an oxalate, to any natural water, is followed after 3 or 4 days by a perceptible clouding, and if the water contained nitrate, this clouding will be found by the metaphenylenediamine test to be *coincident* with the production of a trace of *nitrite*. The air itself, if it gain access to the water, invariably brings germs which produce this incipient reduction. The cloudiness produced in good waters will be longer delayed than that in polluted waters, will be much slighter, and will disappear after a few days, leaving a very slight deposit of dead bacteria. Unless a very small quantity of nitrate was present the reduction to nitrite will not be complete, and the nitrite will eventually renitrify to nitrate. Unless the entering air be carefully filtered, however, a growth of mould may be set up which will hinder this reoxidation and even produce a further reduction.

With more doubtful waters, especially those which contain several grains per gallon of added or original nitrate, the denitrification will proceed farther. Turbidity will be produced in 2 or 3 days, and coincident with this appearance will be that of a trace of *nitrite*. The nitrite, however, will rapidly increase, and in the course of 3 or 4 days more nearly all the nitrate may be reduced to nitrite, so that 10 c.c. of the water will decolorise several cubic centimetres of permanganate, and the metaphenylenediamine test will give an immediate deep orange colour and then a precipitate. During this fermentation, which takes place whether the bottles be full or half full, open or corked, little or no gas will be evolved, and not a trace of ammonia will be produced. Oxalates seem to be equally efficacious with the other substances named in producing this purely nitrous reduction of nitrate; at first, of course, a precipitate of calcium oxalate is caused, but the water is perfectly clear the next day, and gives no reaction for nitrite; on the 3rd or 4th day a fresh turbidity is seen and is signalised by the appearance of nitrite. With these waters the deposit is flocculent, and much more considerable than with the best waters; but the nitrite, after its rapid formation, persists at any rate for some time, although, if there is but little of it, it may soon be used up at the expense of various growths. In corked bottles, half full, a mould will generally be encouraged, and ammonia will be afterwards found.

Other waters again quickly become clouded, and set up a fermentation which ends in total destruction of the nitrate, and is accompanied by evolution of nitrogen gas. If the water contains 4 to 5 grains per gallon nitrogen as nitrate, this will be completely destroyed in about 10 days from the first noticeable turbidity, and minute bubbles of gas will escape during the entire progress of the fermentation; an example of this has already been given. If the water contains very little nitrate originally, perhaps only a few bubbles of gas will be evolved, but the complete destruction of the nitrate instead of the production and persistence of nitrite will mark off this fermentation from the previous one. If, on the other hand, a considerable quantity of nitre, as well as of fermentable organic matter, be added to the water (say as much as 2 grams per litre of each), the fermentation and evolution of gas will go on for, at any rate, 4 or 5 months in a suitable apparatus. I have employed for this purpose an inverted Florence flask, full of water, and corked, with a bent tube of fine bore passing through the cork to allow the escape of liquid as fast as gas accumulates.

Cane-sugar, sodium acetate, and Rochelle salt, employed in parallel experiments with the same water, all provoked this same fermentation; the rapidity was in the order named. When the last two substances are used, an alkaline carbonate is the result. I cannot say whether oxalates will support this fermentation. When the fermentation is very rapid and the water contains nitrogenous organic matter, ammonia is usually found to be present at the conclusion; and the denitrified solution, in the case of bad waters, very easily lends itself to rank growths of various sorts which speedily render the whole liquid thick or ropy. Should hydrogen sulphide, however, be produced by reduction of a sulphate during the fermentation, these growths do not take place. The ammonia formed renitrifies after a considerable time if the liquid be exposed to the air.

Bearing in mind Dr. Angus Smith's observation, that excreta added to solution of nitre produces *this* destructive fermentation, and Gayon and Dupetit's experiments, in which sewage added to nitrated fowl broth and similar decoctions produced the same result, there is some presumption that a well water found to act in this energetic manner may do so because of sewage contamination.

This is confirmed by the fact that the addition of a few drops of fresh sewage to a good well water will cause it to take on this action. Although the gaseous fermentation of nitre *will* take place in bottles only half full of water, and even in vessels fully exposed to air, yet I have little doubt that the exclusion of air is favourable to it. Daylight seems to exert little influence. A circumstance that may prove fatal to such a test is the fact that, according to Dehérain and Maquenne, all soils contain a bacterium which provokes the butyric

fermentation of sugar, and in the presence of nitre a gaseous denitrification is produced very similar to that caused by sewage. So far as my experiments have gone, however, neither good waters nor good waters with even the addition of a *little* soil, will produce this result under ordinary circumstances. In Dehérain and Maquenne's experiments much soil appears to have been used, and they state that the exclusion of air is essential.*

The conclusions arrived at in this paper suggest one or two remarks bearing upon the chemistry of waters and water analysis.

In the first place, what is the nature of the organic matter contained in potable waters?

The soil is the abode of many ferments, some of them having opposed functions, but all lying in wait for suitable conditions which shall encourage one species for a little time until it has done its work and has brought about an alteration favourable in turn to the encouragement of another species. From the soil, these ferments pass into the waters, from which they are not completely removed even by filtration, and the nitric ferment—certainly one of the most subtle of them all—seems little affected by this process. The addition of any ordinary organic matter instantly excites activity in one or other of these ferments, and the effect is soon visible to the eye by the impaired clearness of the water, and to chemical tests by the effect produced on the nitrate of the water.

Now this organic matter need not be by any means that commonly regarded as putrefiable, or even like sugar, of a nature long recognised as easily fermentable. On the contrary, these soil and water ferments do not spare such simple organic compounds as acetates and oxalates, and they attack even such unlikely ones as ethylamine, cyanides, and thiocyanates. The broadest answer then, that I can find to the question asked above, is, that the organic matter of potable waters can be only such organic matter as is nonfermentable, or at any rate not rapidly or easily fermentable; and the conception of rapidly or easily fermentable organic matter must be enlarged so as to include a great number of substances of diverse natures. What two compounds, for example, could exhibit a greater contrast than gelatin and potassium thiocyanate? yet the one is as readily broken down by soil ferments as the other. Indeed, the difficulty is to make out a list of known compounds which are *not* fermentable, especially if they are to be at the same time not fatal to organic life (antiseptics).

The following remarks on the occurrence of inorganic nitrogen in waters apply to well waters more especially; river waters and the water supplies of large towns represent a blend of many conditions.

* Gayon and Dupetit have recently shown that the hydrogen evolved in the butyric fermentation does not reduce nitrates present in the solution.

The normal condition of an unpolluted well water I should state thus (having regard only to the points directly raised in this paper): —Perfectly clear; ammonia and nitrite absent, or present in barely measurable quantities; nitrate always present, but in strictly limited amount.

Ammonia may be present as the result of a putrefactive fermentation of nitrogenous organic matter actually in progress; in which case the water will be more or less cloudy. It may be persisting without sensible alteration during the variable period of inaction of the nitrifying ferment which follows the dying down of the putrefactive ferments—in which case the water may be clear. It may be in process of active nitrification, and a large quantity may disappear *in a few days* with a corresponding increase in the nitrate; this is especially liable to occur in the summer, and should a week elapse between two analyses of the same sample of water some very striking differences in the results would be manifest, although each analysis might be perfectly correct. I am within the mark in stating that a well water may completely nitrify 1 grain per gallon of ammoniacal nitrogen within a week; but it must be remembered that this will not take place immediately after the addition of the ammonia. Even if the presence of the ammonia is not associated with a putrefactive fermentation which delays nitrification, a variable period of quiescence will take place—in fact the *rapid* conversion of ammonia only takes place when nitrification has reached its height.

Finally, ammonia may be present in the stagnant waters supporting confervoid growths, as a bye-product of the reduction of nitrate by various organisms. Ammonia formed by reduction is not of frequent occurrence in well water, however, unless it is accompanied by ammonia resulting from putrefaction.

Nitrite.—"Nitrogen as nitrite and nitrate" has long held a place in water analysts' reports, but nitrite alone is seldom tested for, and still less frequently estimated. Although nitrite is very easily formed by both oxidising and reducing fermentations, it is very rarely present in natural waters except in very minute traces. It will sometimes persist in quantity, and for long periods, in artificially fermented solutions and in water contained in vessels, but in contact with any large quantity of fresh soil it is very rapidly oxidised. It may exist in a water because the conditions do not favour complete nitrification of free ammonia, and in this case the water may be clear; or because of a bacterial reduction of the nitrate, caused by an influx of almost any organic matter; in this case the water is *not* clear.

The reason why nitrite formed by reduction is not often found in well waters is that in most cases the organic matter provoking the reduction consists of sewage, and, as we have seen, sewage contains

bacteria which speedily destroy both nitrate and nitrite, with liberation of nitrogen gas.

If well waters are kept out of contact with soil, nothing is easier than to produce nitrite by nitrification of artificially added ammonia; but the low temperature, extreme dilution of the ammonia, and general contact with soil and air, combine to produce a purely nitric fermentation in most wells and rivers.

An experiment with the recently polluted well water B (p. 664), illustrates this point. This water contained sufficient free ammonia to give an orange *precipitate* with the Nessler test; about 300 c.c. of it was therefore placed in a plugged flask, without any added ammonium chloride, in order to compare the nitrification of the sewage ammonia under the artificial conditions of these experiments with that which takes place *in situ* in the well. Placed in the flask on May 24, 1886, and incubated with the rest of the Bristol waters at 80—85° F., the free ammonia disappeared in less than 22 days, but enough nitrite was formed to give a bright yellow or orange reaction with metaphenylenediamine; 10 days later the nitrite also had disappeared. In the well itself, the water never developed sufficient nitrite to give a recognisable colour with metaphenylenediamine.

Nitrate.—An excessive quantity of nitrate in water is very generally regarded with suspicion; I am not aware, however, that the *absence* of nitrate has been pointed out as a ground of condemnation. Clean rain water and the water of mountain streams often contain but a trace of nitrate; well and river waters *must* however contain more than a trace unless some cause has brought about the destruction of previously existing nitrate. This cause is the access of fermentable organic matter to the water, and in most cases the fermentable organic matter is derived from sewage. When, therefore, a water contains enough mineral matter to demonstrate its percolation through soil, and at the same time is free from nitrate, or contains only a trace barely recognisable by diphenylamine, the occurrence of a destructive fermentation may be inferred. These cases are not uncommon amongst well waters, and the water is generally not perfectly clear—the well water B (p. 664) is an example.

XI. *Period of Incubation of the Nitrifying Organism.*

In all published experiments, including my own, a period of apparent inaction follows the addition of a little soil or nitrifying liquid to a solution prepared for nitrification; this period varies from a few days to weeks or even months, according to the strength of the ammoniacal solution, the quantity of seed used, and other circumstances. At one time I thought that by excluding the tartrate or other fer-

mentable organic matter which encourages the rival denitrifying ferments, I should be able to suppress the incubating period altogether. This can actually be done provided enough seed be used; but to get sufficient or sufficiently active seed it is generally necessary to resort to a first cultivation, during which a true incubating period, or period of growth of the nitrifying organism, is observed. The following examples will explain my meaning. Although the well and river waters used were free from fermentable organic matter, it will be remembered that 150 c.c. laboratory well water required 21 days of incubation before it commenced to nitrify 5 mgrms. NH_3; river water required 7—9 days;* river water + 1 per cent. of soil required 4—5 days; and even a solution containing 150 c.c. distilled water, 5 c.c. NH_4Cl, a few milligrams of K_3PO_4, and 5 per cent. of soil, only commenced nitrifying after 3—4 days. These are periods of true incubation: the less nitrifying ferment there is present, the longer does it take to multiply to an extent sufficient to attack the relatively enormous proportion of ammonia presented to it. But once the ferment is sufficiently developed, it will produce nitrification in a fresh solution *without* incubation, *provided* fermentable organic matter be absent (or perhaps if all reducing organisms can be *rigorously* excluded). When the nitrified solution last-mentioned, for instance, was poured off the 5 grams of soil and replaced by 150 c.c. fresh NH_4Cl of the same strength, nitrification commenced in *less than* 24 *hours*, and lasted 20 days instead of 30. When this was over, the solution was poured away, the wet soil divided into two equal portions, and each of them covered with 50 c.c. of NH_4Cl solution of half the former strength. The bottles were also heated to 80—85°. *To one of them a little sterilised solution of Rochelle salt was added.* The one without tartrate commenced nitrifying in *less than seven hours*, and finished in nine days. Here the suppression of incubation was complete. The tartrated solution, on the other hand, although it showed a trace of nitrite in seven hours, was completely free from nitrite and nitrate on the third day, and nitrification of the added ammonia did not commence for some days later. This represents a period of false incubation; the trace of nitrite at first found proceeded from *reduction* of the trace of nitrate left adhering to the soil from the previous nitrification, and on the third day this reduction had ended in destruction.

The commencement of nitrification in these experiments was taken to be coincident with the first recognisable trace of nitrite (metaphenylenediamine test). I proved by daily testings in a separate

* Thorough aëration of the river water, caused by allowing it to fall through the air in a minute stream several times every day, did not perceptibly shorten this period of incubation.

solution that *soil alone* causes no reduction of nitrate to nitrite; so that the nitrite observed, except in the tartrated solution, really arose from oxidation of the added ammonia.

Even strong solutions of ammonium chloride will commence nitrifying without any appreciable period of incubation if the conditions indicated above are fulfilled. Thus 700 c.c. distilled water containing 267·5 mgrms. ammonium chloride with no addition but 500 mgrms. calcium carbonate and 333 mgrms. washed soil taken from a recently nitrified solution, in three days developed enough nitrite for easy detection.

Appendix.—In a memoir published since the above paper was in manuscript, MM. Gayon and Dupetit (*Recherches sur la réduction des nitrates par les infiniment petits*, Nancy, 1886) examine certain cases of denitrification in an exhaustive manner. After recognising that many different species of microbes will effect the reduction of nitrate to nitrite, and that the presence of fermentable organic matter of any description is the circumstance which determines denitrification under ordinary conditions, they devote the remainder of the treatise to a minute study of two species of microbes, *Bacterium denitrificans*, α and β, which reduce nitrates with the liberation of nitrogen gas, and sometimes nitrous oxide. Both of these organisms were isolated for study by successive cultivations of a drop of sewage in artificial media. In liquids free from nitrate, they behave as aërobic bacteria, and multiply only on the surface of the liquid, forming a zooglœa impermeable to air. It is even possible to cultivate them in liquids containing nitrate without any destruction of the latter, provided a continuous and thorough aëration of the liquid is maintained. But in nitrated liquids protected from the air, or only partially exposed to it, they live at the expense of the oxygen of the nitrate, and effect the complete oxidation to carbon dioxide of the carbon contained in the organic matter introduced into the liquid. And it is only when this organic matter is nitrogenous that any ammonia is formed during the process. Nitrite is at first formed, but is speedily destroyed. By calculation and experiment, MM. Gayon and Dupetit show that the heat produced by oxidation of the organic carbon, *minus* that absorbed by destruction of the nitrate, is a positive quantity, sufficient in fact to raise the temperature of the fermenting liquid several degrees above that of the surrounding air.

LX.—*Detection and Estimation of Iodine, Bromine, and Chlorine.*

By M. Dechan, F.C.S., Lecturer on Chemistry, &c., School of Science, Hawick.

The various methods which have been proposed for the qualitative determination of iodine, bromine, and chlorine, in the presence of each other, are either so complicated or so uncertain, that any simplication of the process of working, which would at the same time yield more accurate results, must be of interest to the analyst. The detection of iodine in the presence of bromine and chlorine has been shown by Cook (Trans., 1885, 471) to be readily accomplished. The presence, however, of small quantities of bromine and chlorine is admitted to be much more difficult of detection. For quantitative purposes, the separation of the halogens is a problem of even still greater difficulty, and is one which up to the present has been but imperfectly solved.

A strong solution of potassic dichromate at the ordinary temperature has little or no action on potassic iodide; if, however, the temperature be raised to the boiling point of the liquid, the iodide is completely decomposed in accordance with the equation $5K_2Cr_2O_7 + 6KI = 3I_2 + 8K_2CrO_4 + Cr_2O_3$, and the whole of the iodine is liberated, whereas bromides and chlorides are not in the least affected. On adding dilute sulphuric acid, and again distilling, the bromine is alone liberated. A simple process of separating the halogens may be based on these facts.

The solution of potassic dichromate which I have found to yield the best results, is prepared by dissolving 40 grams of the salt in 100 c.c. of water. A solution of this strength is without any effect on bromides or chlorides, but the iodides are rapidly decomposed by it. For the purpose of decomposing the bromides and liberating the bromine, a dilute solution of sulphuric acid is added to the dichromate solution. The acid solution is composed of equal parts by volume of acid (1·84 sp. gr.) and water, and should be added to the dichromate solution in the proportion of 8 c.c. of the dilute acid to every 100 c.c. of water originally taken to prepare the dichromate solution. The chlorides are partially decomposed by the acid solution with the formation of chloro-chromic anhydride, CrO_2Cl_2; this, however, is not carried over with the distillate in solutions of the above strength.

For qualitative analysis, the following method has been adopted: a medium-sized boiling tube is fitted with a delivery-tube, bent twice

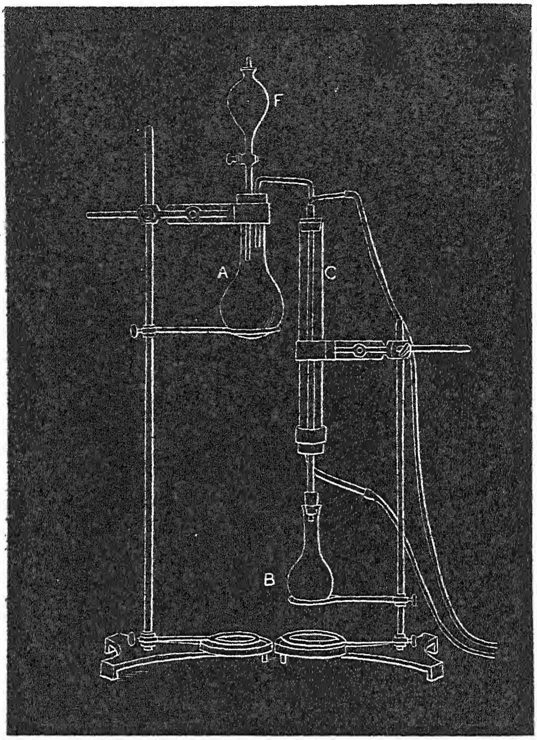
at right angles, one of the limbs of the tube being long enough to reach to the bottom of an ordinary test-tube. The potassic dichromate and water are placed in the tube in the proportions already indicated, together with the substance to be analysed. The contents of the tube are heated, and when ebullition commences, the end of the delivery-tube is dipped beneath the surface of a little water, to which has been added a drop of carbon bisulphide, contained in an ordinary test-tube: the merest trace of iodine is thus shown. The boiling is continued so long as the escaping vapours turn a drop of starch solution blue. Should the boiling be prolonged, care must be taken not to allow the liquid to become concentrated below two-thirds of its original bulk. When the vapours no longer affect the starch solution, the tube is withdrawn from the flame, and a quantity of the dilute acid added in the proportions already stated. The contents of the tube are again boiled, and the escaping vapours tested for bromine by means of a little chloroform, or a solution of potassic iodide and starch. When all the bromine has been evolved, the contents of the boiling tube are rinsed into a clean beaker, diluted with water and tested in the ordinary way for chlorine. For qualitative purposes care must be taken to employ pure potassic dichromate; this ought to be specially tested for chlorine before being used.

For quantitative determinations the following arrangements must be provided for: prolonged boiling, for about one hour, with some means of keeping the volume of liquid at not less than two-thirds of its original bulk without requiring to take the apparatus apart. The reason why the liquid must not be concentrated beyond the point indicated, is, that in liberating the bromine with the aid of the dilute acid traces of chlorochromic anhydride are given off if the liquid becomes too concentrated, and this coming into contact with the potassic iodide solution liberates some of the iodine.

The accompanying sketch shows the arrangement of the apparatus used for quantitative determinations :—

The flask A has a capacity of 150 c.c., the separating funnel F serves for keeping up the volume of liquid, and also for adding the dilute acid. The flask B attached to the lower end of the condenser C contains the potassic iodide solution for the purpose of dissolving the liberated iodine. It has a capacity of about 100 c.c.

The details of the process are as follows: 100 c.c. of water, 40 grams of the potassic dichromate, and about 0·4 gram of the substance to be analysed are placed in the flask A; the apparatus is then put together as shown in the sketch, the contents of A heated to boiling, and the iodine which distils over is received in the flask B. After boiling for 10 minutes, the flask B may be removed, and a test-tube containing a solution of starch inserted in its place. The boiling



is continued until a drop of starch solution is no longer turned blue by the condensed vapours. When this occurs, the burner is removed for a moment, and 8 c.c. of the dilute acid added by means of the separating funnel. The contents of B, together with the other parts of the iodine distillate, are rinsed into a beaker, and the iodine determined by means of decinormal thiosulphate solution.

The flask B is now charged with a fresh solution of potassic iodide, attached to the condenser as before, and the distillation continued. When all the bromine is driven over—which is known by the condensed vapours no longer turning a solution of potassic iodide and starch blue—the quantity of iodine liberated by the bromine is estimated as before, and the equivalent amount of bromine determined by calculation.

The contents of A are rinsed into a beaker and diluted with water, which decomposes the chlorochromic acid formed into chromic acid and hydrochloric acid. Nitric acid is now added, and the chlorine precipitated with argentic nitrate in the usual way.

Comparing the process herein described with those already published, it will be readily admitted to be more easy of application, and will, I feel sure, be found to be capable of yielding more regular and accurate results. Those who require to determine the quantity of bromine in kelp liquors, for which no process with any pretension to accuracy has as yet been proposed, will find the one here described both expeditious and trustworthy.

The following results obtained in the analysis of three mixtures will give some indication as to the capabilities of the process.

The iodine, bromine, and chlorine were present in each case as iodides, bromides, and chlorides, and the quantity of the halogen present in each salt was determined gravimetrically before preparing the mixtures:—

No. of mixture.	Chlorine.		Bromine.		Iodine.	
	Taken.	Found.	Taken.	Found.	Taken.	Found.
I........	0·0123	0·0122	0·0126	0·01254	0·01443	0·01441
II........	0·056	—	0·0252	0·0250	0·0288	0·02833
III........	0·194	—	0·0504	0·05009	0·0576	0·05628

The chlorine in mixture II and III was not determined; and if the apparatus had been constructed so as to do away with the use of cork in the fittings, the results would, I feel sure, have been nearer those demanded by theory.

LXI.—*Note on the Vapour-densities of Chloral Ethyl-alcoholate.*

By William Ramsay, Ph.D., and Sydney Young, D.Sc.

In a memoir on "Evaporation and Dissociation" shortly to be published in the *Transactions of the Royal Society*, the results of determinations of the temperatures of volatilisation, vapour-pressures (or dissociation-pressures), and vapour-densities of chloral ethyl-alcoholate are described, and also similar constants for chloral hydrate and chloral methyl-alcoholate. These results appeared to warrant the conclusion that the alcoholates are more stable than the hydrates, and that some light might be thrown on the effects of temperature and

pressure on the dissociation of gaseous compounds by a more extended study of the vapour-densities of these compounds.

Although it has been found that the dissociation of the vapour of chloral ethyl-alcoholate under the possible conditions of experiment is never very far from complete, and that it is impossible to obtain very concordant observations, yet we think a short account of the experimental results may be of interest.

The vapour-density determinations were made in a Hofmann's apparatus, modified, as described in a memoir on "The Thermal Constants of Ether" recently communicated to the Royal Society, so as to allow of pressure, volume, and temperature being altered at will.

The results are as follows:—

Weight of Substance = 0·01200 gram.

Pressure of Alcohol Vapour 220 mm. (reduced to 0°); Temp. 50° (air thermometer).

Pressure.	Volume.	Vapour-density.	Pressure.	Volume.	Vapour-density.
14·2 mm.	172·25 c.c.	49·23	24·5 mm.	89·4 c.c.	54·98
16·1 "	149·0 "	50·20	24·8 "	79·35 "	61·20
19·45 "	121·4 "	50·98	24·85 "	69·9 "	condensed.
23·3 "	100·95 "	51·43	—	—	—

Pressure of Alcohol Vapour 350·3 mm.; Temp. 60°.

Pressure.	Volume.	Vapour-density.	Pressure.	Volume.	Vapour-density.
15·05 mm.	165·55 c.c.	49·83	37·15 mm.	64·9 c.c.	51·50
22·0 "	111·75 "	50·50	42·05 "	56·2 "	52·53
32·05 "	75·5 "	51·31	46·1 "	48·2 "	55·86

Pressure of Alcohol Vapour 541·2 mm.; Temp. 70°.

Pressure.	Volume.	Vapour-density.	Pressure.	Volume.	Vapour-density.
16·18 mm.	163·9 c.c.	48·25	51·10 mm.	48·05 c.c.	52·08
22·30 "	117·25 "	48·91	61·50 "	39·00 "	53·31
29·00 "	88·75 "	49·68	80·95 "	29·0 "	54·47
35·85 "	70·00 "	50·96	83·5 "	23·95 " condensed.	63·94
45·45 "	55·0 "	51·16			

Pressure of Alcohol Vapour 755·65 mm.; Temp. 78·15°.

Pressure.	Volume.	Vapour-density.	Pressure.	Volume.	Vapour-density.
16·15 mm.	164·9 c.c.	49·16	20·95 mm.	127·0 c.c.	49·09

Pressure of Alcohol Vapour 747·35 mm.; Temp. 77·9°.

Pressure.	Volume.	Vapour-density.	Pressure.	Volume.	Vapour-density.
16·7 mm.	164·85 c.c.	47·52	54·55 mm.	48·2 c.c.	49·76
26·7 „	100·65 „	48·59	—	—	—

Pressure of Alcohol Vapour 745·5 mm.; Temp. 77·8°.

Pressure.	Volume.	Vapour-density.
71·65 mm.	35·05 c.c.	52·10

Pressure of Alcohol Vapour 753·2 mm.; Temp. 78·1°.

Pressure.	Volume.	Vapour-density.	Pressure.	Volume.	Vapour-density.
72·2 mm.	34·85 c.c.	51·98	118·65 mm.	20·2 c.c.	54·61
94·35 „	25·9 „	53·56	—	—	—

Weight of Substance = 0·07088 gram.

Pressure of Chlorobenzene Vapour 134·15 mm.; Temp. 78°.

Pressure.	Volume.	Vapour-density.	Pressure.	Volume.	Vapour-density.
91·1 mm.	164·5 c.c.	51·59	112·95 mm.	130·0 c.c.	52·64
105·85 „	139·6 „	52·31	117·5 „	121·8 „	54·00

The following determinations are reproduced from the paper referred to:—

Weight of Substance = 0·02066; Temp. 78·35°.

Pressure.	Volume.	Vapour-density.	Pressure.	Volume.	Vapour-density.
111·0 mm.	38·42 c.c.	52·88	122·9 mm.	34·68 c.c.	52·95
117·7 „	36·28 „	52·82	—	—	—

Weight of Substance = 0·07088 gram.

Pressure of Chlorobenzene Vapour 208·35 mm.; Temp. 90°.

Pressure.	Volume.	Vapour-density.	Pressure.	Volume.	Vapour-density.
97·3 mm.	162·2 c.c.	50·06	185·55 mm.	82·9 c.c.	51·97
121·15 „	129·4 „	50·99	214·5 „	70·25 „	53·04
148·35 „	105·1 „	51·27	224·6 „	65·0 „ (condensed)	53·83
171·6 „	90·05 „	51·73			

Pressure of Chlorobenzene Vapour 292·75 mm.; Temp. 100°.

Pressure.	Volume.	Vapour-density.	Pressure.	Volume.	Vapour-density.
138·2 mm.	119·2 c.c.	49·86	334·6 mm.	46·4 c.c.	52·91
196·05 „	82·2 „	50·97	355·05 „	43·1 „	53·81
263·85 „	60·0 „	51·89	—	—	—

Pressure of Chlorobenzene Vapour 402·55 mm.; Temp. 110°.

Pressure.	Volume.	Vapour-density.	Pressure.	Volume.	Vapour-density.
106·6 mm.	158·6 c.c.	49·89	461·95 mm.	34·8 c.c.	52·4
140·85 „	120·0 „	49·90	530·4 „	29·3 „	54·24
201·3 „	83·0 „	50·48	578·2 „	24·5 „ (condensed)	59·54
324·6 „	50·7 „	51·25			

Pressure of Chlorobenzene Vapour 754·5 mm.; Temp. 131·8°.

Pressure.	Volume.	Vapour-density.	Pressure.	Volume.	Vapour-density.
114·05 mm.	163·0 c.c.	48·67	301·6 mm.	59·55 c.c.	49·64
143·45 "	126·8 "	49·01	428·5 "	41·5 "	50·12
209·55 "	86·6 "	49·13	595·75 "	29·5 "	50·72
295·65 "	61·1 "	49·36	—	—	—

The calculated vapour-density is 96·56. If dissociation were complete, it would therefore be 48·28.

Besides the ordinary corrections for the vapour pressure of mercury and the heated column of mercury, the small quantity of air in the tube was estimated and allowed for in each calculation.

That the results are not so concordant as with stable substances is probably to be accounted for by the fact, that when volume or temperature is altered, equilibrium is not at once established. After increasing the volume or raising the temperature, the first readings of pressure are invariably too low, and the vapour-densities consequently too high; observations were therefore made from time to time until no further change could be detected. When the volume was decreased or the temperature lowered, the reverse effect was observed.

The results were plotted on curve paper, but since the total variation of density was only from 48 to about 54·5, and since the difference in the observed vapour-densities under the same conditions of pressure and temperature amounted occasionally to more than a unit, it was impossible to determine satisfactorily the position of the curves representing the relation of vapour-density to pressure and temperature. It is, however, obvious from the results that at constant pressure dissociation increases, and the vapour-density is therefore lowered by rise of temperature, whilst at constant temperature a similar effect is produced by lowering the pressure.

It was also found impossible to discover with certainty the alteration of the density of the saturated vapour with fall of temperature, which was readily ascertained in the case of alcohol, ether, and even of acetic acid by drawing a curve to pass through the points of intersection of the isothermal lines with the horizontal lines representing vapour pressures or of the isobars with the horizontal lines denoting boiling points or temperatures of volatilisation. The chief cause of this difficulty is the fact, noticed to a less extent with acetic acid, but not at all with alcohol and ether, that when volume is decreased condensation begins before the pressure has reached its maximum. It may be

stated, however, that between 50° and 100° the density of the saturated vapour ranges between 52° and 55°, and that there is no appearance of a rise of density with fall of temperature, but that, on the contrary, the density of the saturated vapour appears to be distinctly lower at 50° than at 70°. Calculating the percentage number of molecules decomposed by means of the equation

$$p = 100\left(\frac{D - d}{d}\right),$$

where D is the calculated and d the found density, it appears that in no case are there fewer than 75 per cent. of the total number of molecules of chloral ethyl-alcoholate decomposed.

LXII.—*Water of Crystallisation.*

By W. W. J. Nicol, M.A., D.Sc., F.R.S.E., Lecturer on Chemistry, Mason College, Birmingham.

A paper with the above title appears on pp. 411—432 of this volume of the Society's Transactions; and in it Professor Pickering endeavours to show that experiment does not really warrant the generally accepted view that in the heptahydrated magnesian sulphates *one* of the water molecules (water of constitution) stands in a relation to the salt different from the other six. In the course of the paper, Professor Pickering adversely criticises the deductions made by me from experiments on the molecular volume of dissolved salts (*Phil. Mag.*, 1883, 121; 1884, 179). These deductions were:—

That water of crystallisation occupies the same volume as solvent water when the salt is dissolved; but on the other hand water of constitution has a molecular volume markedly different from that of solvent water, consequently it is probable that water of crystallisation does not exist in solution, and that water of constitution does remain attached to the salt.

The first ground of complaint is that the data are insufficient. But my results for water of crystallisation are not only numerous, comprising 23 pairs of salts, but are supported by the results of other experimenters, amongst others by the density "moduli" of Favre and Valson, by the similar work of Bender, by the work of Groshans based on the experiments of Schiff, Kremers, Gerlach, and many others; and, finally, by that of Ostwald on the volume change

on neutralisation of a large number of acids; so completely is this established that it is stated in Meyer's *Modernen Theorien der Chemie* (1884, 452, *et seq.*) and in Ostwald's *Handbuch* (p. 387). There is thus no doubt that the volume of a salt in solution is a value made up of two constants, *one* for the metal, the *other* for the salt radicle. Water of crystallisation has no place here. With one class of salts, and only with a section of that class, has an exception been found to the above rule. This class is that of the sulphates: so long as sulphates containing no water of constitution are concerned, the law holds good, there is a constant difference between their volume and that of other salts of the same metals. But the section of the sulphate class known as the magnesian sulphates show a marked difference, they have uniformly a greater volume and the differences are consequently less. An explanation of this is to be found, I still think, in the presence of the constitutional water molecule; at least no other explanation has been attempted by Professor Pickering, who complains that my results are not numerous enough, and that other classes of sulphates should have been examined. Professor Pickering has not considered how many soluble sulphates there are. As it happens there are at the very most only 24 available for this form of experiment. Of these I have examined 11, the remainder are nearly all sulphates of the rare metals.

In my previous papers I have expressed my belief that we have no evidence at all that the salt exists in water as a hydrate, definite or indefinite; and I pointed out that the heat of hydration so commonly cited as a proof has in reality nothing to do with the question. For though there is no doubt that the act of dissolution of a dehydrated salt consists first in the formation of a hydrate, yet that hydrate is *solid*, and the thermal results do not bear on the question of what is the fate of this hydrate on solution. I ventured to suggest that it is possible that the solid hydrate is decomposed on solution. This Professor Pickering says is impossible, but it does not seem to have appeared impossible to Berthelot or Thomsen, both of whom discuss the question; as a matter of fact, the question has not yet been really touched upon, all those who have discussed the point having been misled by the heat of hydration of the *solid* salt. I hope, however, in a subsequent paper, to show conclusively from thermochemical results that water of crystallisation does not exist in solution.

Professor Pickering's remarks on the theory of solution proposed by me some years ago cannot be spoken of here, with the exception of one point which I cannot pass over in silence: surely Professor Pickering does not imagine that he has made a point against the theory when he writes, "It is scarcely necessary to point out that no amount of attraction, chemical or otherwise, can of itself produce the

least *particle* of heat; it is only the actions which result from this attraction which can do so."

The concluding paragraph of Professor Pickering's remarks on my work shows that he has failed to grasp the nature of my argument regarding water of crystallisation, based on a comparison of the molecular volumes of the solutions; and he is wrong when he states that the specific heat and specific volume in many cases of water of crystallisation in the solid state is the same as that of solid water. The specific heat in a few instances, and the specific volume in one or two, is the same as that of solid water; in all the others it is markedly different. I may say in conclusion, when Professor Pickering shows that the difference in molecular volume of solid salts of two metals with various acids is a constant quantity, no matter whether water of crystallisation be present or not (if present its volume as solid water being deducted), then I shall be quite ready to admit that it is possible that my experiments on the molecular volumes of dissolved salts *may* not be conclusive evidence against the presence of water of crystallisation in solutions.

LXIII.—*Phenylsulphonic Anhydride.*

By J. L. H. ABRAHALL, Magdalen College, Oxford.

IN the *Annalen* (**223**, 238), Hübner describes a series of endeavours to prepare the anhydride of phenylsulphonic acid. His last attempt, in which he heated silver phenylsulphonate with phenylsulphonic chloride, was partly successful, but he lost the result of his labours by extracting the product with ether, which combined with the anhydride to form ethylic phenylsulphonate.

In ignorance of Hübner's work, Professor Odling suggested the preparation of this substance by the method mentioned above, and its extraction with chloroform. About 30 grams of the chloride, which, as Mr. Gossage has found, can be easily obtained in a state of purity (m. p. 18·5°) by distilling the washed crude product under reduced pressure (8 mm. of mercury), was mixed with a slight excess of the silver salt prepared from sodium phenylsulphonate and silver nitrate, the two substances having been previously dried with great care. The mixture was heated at 160—180° for 20 hours, and the greyish-brown solid formed was extracted with chloroform. On evaporating the brown solution, it deposited fine prismatic crystals, which were

obtained almost colourless by recrystallisation. After crushing them between porous plates the sulphur was estimated by Carius' method:—

I. 0·2032 gram substance yielded 0·3114 gram barium sulphate,
II. 0·1890 " " 0·2761 " "

corresponding with 21·07 and 20·63 per cent. sulphur, the theoretical percentage for $(C_6H_5SO_2)_2O$ being 21·48.

As the substance is extremely deliquescent, it was impossible to weigh it without some absorption of water from the air. This will probably account in part for the somewhat low percentage of sulphur.

It melts at 54°, and when strongly heated a viscid liquid distils over, which deposits crystals on cooling; the greater part, however, is decomposed with formation of a black tarry matter.

It combines immediately with water, and gradually, as Hübner has shown, with ether. With phenol it forms a viscid liquid which I have not yet further examined.

It is remarkable that this anhydride corresponds with sulphur trioxide much more closely than the sulphonic chloride does with the chlorides of sulphuric acid, phenylsulphonic chloride being inappreciably acted on by water and only slowly decomposed by dilute alkalis. In this respect it contrasts with the anhydrides of the carboxylic acids, which are more stable in presence of water than their corresponding chlorides.

I must gratefully acknowledge the help which I have received from Mr. A. M. Gossage, of Magdalen College, in the preparation of this substance.

LXIV.—*On the Action of Hexabromacetone on Urea.*

By Alfred Senier.

Several years ago, by acting on urea with hexabromacetone, Herzig (*Ber.*, **12**, 170) obtained two acids which he named respectively α- and β-cyanuric acid. In many respects both these compounds behave like ordinary cyanuric acid, but certain differences were observed which it was thought indicated that they were distinct isomeric substances.

The attention of chemists has recently been directed to the question of the constitution of ordinary cyanuric acid, as to whether it is to be regarded as iso or normal, and it seemed at least possible that a

further study of Herzig's acids might furnish the desired standpoint from which to elucidate this problem. With this end in view, I repeated Herzig's experiments, and obtained what seemed to be two cyanuric acids in the manner he has described. When a mixture of urea and hexabromacetone is heated to a temperature above 150°, bromoform and bromide of ammonium are formed, and when the mixture is heated further to 160° or to 170—180° it then yields to water in the one case the β-, and in the other the α-cyanuric acid.

During the preparation of these acids, however, I was led to doubt whether they really differed from ordinary cyanuric acid. There is no very notable dissimilarity between the method employed by Herzig and that by which the ordinary acid is prepared. All three acids are formed by the action of heat on urea. The temperature, too, which Wöhler observed as that corresponding to the conversion of urea itself into ordinary cyanuric acid, 150—170°, includes the temperatures made use of by Herzig.

It is well known that if chlorine is used as suggested by Würtz (*Annalen*, **64**, 307), or hydrochloric acid as employed by De Vrij (*Annalen*, **61**, 248), the ammonia is removed more readily, being eliminated in the one case as nitrogen and hydrogen chloride, and in the other as ammonium chloride. In Herzig's experiment, hexabromacetone seems to act in an analogous manner to these reagents, and to remove the ammonia as tribromacetamide according to a reaction observed by Weidel and Gruber (*Ber.*, **10**, 1145), thus—

$$CBr\cdot CO\cdot CBr_3 + NH_3 = CBr_3\cdot CO\cdot NH_2 + CHBr_3.$$

No doubt it may be conceived that the hexabromacetone acts in another way, forming bromoform and cyanuric acid, thus—

$$CO{<}^{CBr_3}_{CBr_3} + NH_3 = 2CHBr_3 + CONH,$$

but of this there is no experimental evidence, and even if it is the fact, the resulting acid would be the ordinary cyanuric acid.

Let us now see whether a careful comparison of the properties said to distinguish Herzig's acid with the corresponding properties of ordinary cyanuric acid, causes the doubt which already arises to disappear, or whether as we proceed it becomes more and more defined and rises to certainty.

The properties of the α-acid on which Herzig chiefly relies as differentiating it from ordinary cyanuric acid are :—I. The solubility in alcohol. II. The amount of water of crystallisation. III. The composition of some of its salts.

I. *Solubility in Alcohol.*

Herzig finds the solubility of ordinary cyanuric acid in 100 parts of alcohol at 22° to be 0·349 part, and that of his α-acid to be 0·556 part. In other words, the α-acid is about one and a-half times as soluble as ordinary cyanuric acid. It is remarkable that, notwithstanding this small difference, only a single determination should have been made. My experiments with ordinary cyanuric acid leave little room for doubt that its solubility in alcohol is influenced considerably by small variations in the experimental conditions.

Six determinations made at temperatures very close to that of Herzig's experiment, give me the following numbers which are seen to exhibit considerable differences:—

I.	II.	III.	IV.	V.	VI.	Mean.
0·088	0·095	0·090	0·090	0·100	0·110	0·095

These results were obtained by allowing hot solutions to cool and then remain with occasional agitation for one or two days. They indicate, on the whole, that the solubility of cyanuric acid in alcohol is less than one-third of that found by Herzig; but the numbers are not as concordant as is usual in such estimations. This is explained by the tendency to form supersaturated solutions in alcohol, which, as will be seen from the next experiments, is clearly characteristic of cyanuric acid. Hot saturated solutions were prepared, and the amount of acid held in solution was determined from time to time. At 22—23° 100 grams of alcohol retained in solution—

	Experiment I. gram.		Experiment I gram.
After two hours....	0·192	After one day....	0·122
After two days.....	0·074	After two days ..	0·082
		After three days..	0·090
		After four days..	0·075

It is seen that on standing the solution contains less and less cyanuric acid. If we take the mean of these numbers, the solubility of cyanuric acid in 100 parts of alcohol is 0·106 part. This is, however, a somewhat higher figure than that resulting from the previous determinations (0·095). As the mean of the whole 12 experiments the solubility of cyanuric acid in 100 parts of alcohol at 21—24° is 0·100 part, whilst from one experiment Herzig concludes that its solubility is 0·349 part. Herzig thus finds the solubility to be more than three times as great as my experiments indicate. If the relation of my mean result for ordinary cyanuric acid to Herzig's number, on

the one hand, be compared with that of the numbers found by Herzig for the ordinary, and the α-acids on the other, thus—

$$0{\cdot}100 : 0{\cdot}349 \text{ and } 0{\cdot}349 : 556,$$

then it is evident that the ratio of difference between two observations of the solubility of the ordinary acid is greater than that between the ordinary and the α-acid as given by Herzig. Under these circumstances, a small difference in solubility of two substances can be accepted only very reluctantly as evidence of difference of constitution.

The solubility of cyanuric acid which, in accordance with Herzig's experiment, has found its way into chemical literature (for example, see Beilstein, *Handbuch Org. Chem.*, 2nd Ed., 1006), is therefore too high. If from the twelve experiments I have made, two which are clearly cases of supersaturation are removed, the mean of the remaining ten, 0·09, may be taken as very accurately representing the solubility of the ordinary cyanuric acid in 100 parts of alcohol at 21—24°.

In the next place the relative solubility of the ordinary acid and of Herzig's α-acid must be examined.

The difference of solubility in the case of these two acids as observed by Herzig, and as the result of two experiments of my own, is as follows:—

	Herzig.	Senier. I.	Senier. II.
Ordinary cyanuric acid	1·00	1·00	1·00
Herzig's α-acid	1·59	2·15	1·22

The solubility of the ordinary acid is taken as unity for purposes of comparison. In agreement with Herzig, I find the α-acid more soluble than the ordinary acid. But although in my first experiment it is more than twice as soluble, in my second experiment its solubility is not much greater than that of the ordinary acid.

It was observed by Herzig that his α-acid could not be converted into a salt and separated therefrom without being changed into the ordinary acid. Regeneration from a barium salt gave him an acid having the same solubility in alcohol as the ordinary acid. I have repeated the observation and can confirm this statement, thus:—

	Herzig.	Senier.
Ordinary cyanuric acid	1·00	1·00
α-Acid regenerated from a barium salt	0·97	1·10

The most probable explanation of these observations is that minute quantities of foreign substances are present which are sufficient to

increase the solubility of the acid. The purer the acid the more it approaches to the solubility of ordinary cyanuric acid. Conversion of the acid into a salt and regeneration therefrom does not appear to be a process of intermolecular change, but simply a method of purification. If this is true, then the solubility of the α-acid should be reduced when it is purified by recrystallation, for instance, from alcohol. Here are the results of some experiments to determine this compared with the numbers already obtained:—

Ordinary cyanuric acid.	α-Acid.			
	Crystallised from water.	Regenerated from barium salt.	Recrystallised from alcohol.	
			I.	II.
1·00	2·15	1·10	1·15	1·09

Recrystallisation from alcohol itself, then, it is evident, is enough to so purify the α-acid that its solubility in alcohol is reduced very closely to that of ordinary cyanuric acid.

Numerous attempts have been made to discover the impurity the presence of which is the cause of the difference in solubility observed in the case of the acid prepared by the use of hexabromacetone. These inquiries have not, however, led to a perfectly satisfactory conclusion. It is deserving of mention, nevertheless, that when cyanuric acid itself is recrystallised from a solution containing small quantities of biuret, its solubility in alcohol is much increased.

Herzig's observation that fuming nitric acid also converts the α- into the ordinary acid is quite in accordance with the explanation to which I have been led of the behaviour of the α-acid when regenerated from a salt or recrystallised from alcohol, namely, that both these processes are cases of simple purification. This very method was employed long ago by Liebig and Wöhler (*Berz. Jahresbericht*, **11**, 83) as a means of purifying ordinary cyanuric acid. These observers dissolved the crude cyanuric acid in hot oil of vitriol, and to the solution added nitric acid, afterwards precipitating the pure cyanuric acid by water.

II. *Water of Crystallisation.*

The proportion of water held by crystals of ordinary cyanuric acid was determined by Liebig and Wöhler (*Pogg. Ann.*, **20**, 369). When the acid is freshly recrystallised and pressed between paper, it contains 21·8 per cent. of water, corresponding to two molecules. Herzig found in the case of his α-acid only one molecule. His results

are 11·73 and 12·13, corresponding very well with one molecule, which requires 12·24 per cent.

Repeating this experiment with a specimen of the α-acid which I prepared, I found, after freshly recrystallising from water and drying between paper, that it contained 17·6 per cent. water, which was given off at 120°. This specimen was then recrystallised from alcohol, and again from water, when its power of combining with water had risen very nearly to that of the ordinary acid. It contained 19·9 per cent. of water, whereas a determination in the case of the ordinary acid gave me 20·6 per cent. Thus by purification it is seen that the percentage of water of crystallisation which the acid is capable of fixing increases until a number is reached not far removed from that given by the ordinary acid.

III. *Composition of some of its Salts.*

1. *Silver Salts.*—Herzig describes two silver salts of his α-acid. A complete analysis of the one led him to give it the formula

$$(C_3N_3)<^{(OAg)_2}_{(ONH_4)},H_2O,$$

which requires 57·14 per cent. of silver. This is probably, as Herzig himself remarks, the same salt that Wöhler (*Annalen*, **62**, 244) prepared, but to which the somewhat different formula

$$(C_3N_3)<^{(OAg)_2}_{(ONH_4)},NH_3$$

is ascribed, which is based, however, merely on a silver determination. This formula requires 57·29 per cent. of silver.

A trisilver salt of the ordinary acid of the composition

$$(C_3N_3)(OAg)_3,H_2O,$$

which requires 69·23 per cent. of silver, was prepared by Liebig (*Annalen*, **62**, 123), and afterwards by Wöhler (*Annalen*, **62**, 245). Now following the method of Liebig, Herzig obtained in the case of the α-acid salts containing from 57 to 59 per cent. of silver, and this is noted as characteristic of the α-acid.

I have repeated this experiment and have obtained salts with various proportions of silver both from the α- and the ordinary acid. By the careful employment of an excess of ammonia, according to Liebig's method, I obtained, however, from both acids the trisilver salt, as the following analytical numbers indicate :—

	Theory.	Silver salt of cyanuric acid.	Silver salt of α-acid.
Silver	69·23	69·5	68·7

When the ammonia is not in excess throughout the operation, salts

are produced containing a less proportion of silver. Such salts were observed by Wöhler in the case of cyanuric acid and Herzig's salts the α-acid probably belong to this class. One which I obtained gave me 58·1 per cent. of silver.

2. *Barium Salts.*—Wöhler (*Annalen*, **62**, 251) discovered monobarium cyanurate, which he prepared by dropping a solution of barium hydroxide into a boiling solution of cyanuric acid until, the still liquid remaining acid, the first permanent cloudiness appears. The solution is then kept at 60° for several hours, when the salt is precipitated in beautiful crystals. With ordinary cyanuric acid, Herzig working in this manner obtained Wöhler's salt, $C_3N_3(Oba)(OH)_2 + H_2O$.

Herzig's analysis gave—

	Theory.	Experiment.
Barium	31·93	29·72

Now the same experiment in the case of the α-acid led to a different compound, and this is regarded by Herzig as a characteristic property of this acid. The salt obtained contained 41·29 per cent. of barium, corresponding to the formula $C_3N_3(Oba)_2(OH) + 4H_2O$.

But repeating this experiment I arrived at results which are in accord with the general outcome of my previous experiments. I have found when operating with the α- as well as with the ordinary acid, that the same monobarium salt is formed which Wöhler first observed. Thus I obtain the following numbers :—

	Theory.	Cyanuric acid.	α-Acid recrystallised from alcohol.
Barium	31·93	31·73	29·77

The percentage of silver which my α-barium salt contained is the same as that found by Herzig in the salt of the ordinary acid.

By the use of larger proportions of barium hydroxide salts richer in barium are easily produced. From the α-acid I have prepared salts or mixtures of salts containing 41·4 per cent. and 50·23 per cent. of barium, and from the ordinary acid one containing 45·4 per cent.; both these salts and Herzig's salt, which gave 41·29 per cent. of barium, are very probably mixtures.

The doubt which was felt during the preparation of this α-acid as to whether it is to be looked on as a distinct isomeride of ordinary cyanuric acid or not, has gradually become stronger, and the conclusion to which I am led by the whole investigation is that the acid produced by the action of hexabromacetone and heat on urea and known as Herzig's α-cyanuric acid, is identical with ordinary cyanuric acid.

Note on β-Cyanuric Acid.—This acid is produced in the same reaction as the α-acid, but at a somewhat lower temperature. Whilst

the α-acid requires a temperature rising to 180°, the β-compound is formed between 150—160°. It is more soluble in alcohol than the α-acid, but Herzig gives no determination of its solubility. It crystallises from water in anhydrous crystals. Further, it is distinguished from both the α- and the ordinary acid by not giving cyanic acid when heated, and by not forming cyanuric chloride when treated with phosphorus pentachloride. Finally, when dissolved in soda solution and the solution warmed, it does not give the sparingly soluble trisodium salt, which, as pointed out by Hofmann (*Ber.*, 3, 769), is so characteristic of ordinary cyanuric acid.

My experiments give me somewhat different results. I have undoubtedly obtained cyanuric chloride by the action of phosphorus pentachloride. This I have isolated from the crude product of the reaction, and found it to melt at 144°. Moreover, it is easy with my specimen of the β-acid to obtain the difficultly soluble trisodium salt. That it is really the β-acid described by Herzig is proved by the fact that it did not give cyanic acid when heated in a small tube, a test which never fails, even with small quantities, in the case of pure cyanuric acid. Whether, therefore, this β-acid is a distinct isomeric compound cannot as yet be decided with certainty, although the previous work on the α-acid renders this improbable, and a final judgment must await further experiments.

University Laboratory,
Berlin, June, 1886.

LXV.—*On the Measurement of the Electromotive Forces produced by the combination of Cadmium and Iodine in Presence of Water.*

By A. P. Laurie, B.A., B.Sc.

In the March number of the *Philosophical Magazine* for this year, I published a paper on the "Electromotive Forces developed by the Combination of Zinc and Iodine." Instead of completing those experiments, I have taken up the reaction between cadmium and iodine on account of the greater ease with which cadmium iodide is manipulated. The following is an account of my preliminary experiments on this reaction, and the results which I think may be deduced from them.

As is well known, cadmium and iodine combine in the presence of water to form cadmium iodide, which dissolves. Just at the moment of combination there is a difference of electric potential

between the cadmium and the iodine atom, which we can measure by an arrangement which I shall presently describe. This difference of potential is modified by the surrounding conditions. In the first place, we may consider that it is made up of two parts, due respectively to the combination of the cadmium and iodine, and to the solution of the resulting molecule in the water.

Let us first consider that part which is due to the solution of the resulting molecule. If we imagine the reaction to be going on, we evidently have cadmium iodide accumulating in the water present, until at last we may suppose that the water becomes saturated with the salt. When this state is reached, it is evident that there is no further difference of potential between the salt and the water, that this factor of the whole difference of potential has disappeared. No doubt then this portion of the difference of potential has been diminishing from the beginning of the reaction, but it may diminish in two ways. If on the one hand there are any definite compounds formed between the salt and the water, we should expect on passing through the strength of solution corresponding with such a compound to have a sudden change in the difference of potential. If on the other hand no such compounds are formed, but the difference of potential between the salt and the water is a continuous function of the salt already in solution, we should expect the potential to fall off along a continuous curve, flattening as we approached a saturated solution.

Let us now consider the other part of the reaction, namely, the combination of the cadmium and iodine. The cadmium remains a solid metal throughout the reaction, and we may therefore suppose it to be uninfluenced by changes in the solution. The iodine is very slightly soluble in pure water, but is increasingly soluble as the amount of cadmium iodide in solution is increased. There is probably then a difference of potential between the iodine and the cadmium iodide, this difference of potential diminishing as the amount of iodine present in a given solution is increased, and finally disappearing when the solution is saturated with iodine. This difference of potential must evidently diminish the difference of potential due to the combination of the cadmium and iodine, as the iodine has to be torn from its solution in cadmium iodide. We may, however, consider that when the solution is saturated with iodine, the iodine is then free to combine with the cadmium.

We should expect then that if we increase the amount of iodine present in a given solution, the difference of potential will increase between the cadmium and iodine, and in this case also it will increase in jumps if we pass through any compounds of cadmium iodide and iodine; but if there are no such compounds, the difference of potential

between the cadmium and iodine will increase along a continuous curve, the increase, however, becoming less rapid as we approach the saturation of the solution with iodine.

We can, however, diminish this difference of potential in another way. If we suppose a given solution to be saturated with free iodine, and we then add more solid cadmium iodide so as to increase the amount of cadmium iodide in solution, we shall immediately diminish this difference of potential, because we are now no longer dealing with a liquid saturated with iodine; the liquid is capable of dissolving a great deal more iodine, and consequently a difference of potential has been set up between the iodine and the cadmium iodide.

I have explained in my Zinc-Iodine paper how, by integrating such a curve as one of those above described, we can obtain a measure of the whole electrical energy produced by the reaction, so that I need not enter into it here. With a view to measuring these differences of potential I have devised the following voltaic cell.

A cadmium plate and a platinum wire are immersed in a solution of cadmium iodide containing a little free iodine. On connecting the cadmium and platinum plates a current passes through the cell, the cadmium combining with the free iodine to form cadmium iodide, which dissolves in the water present. It is hardly necessary to explain that it is the free iodine round the *platinum* wire which is used for this combination. On connecting this cell with a Thomson quadrant electrometer, I could measure its electromotive force against a Latimer Clark cell, the electrometer reading to 0·005 of a volt. In every case two cells in series were used, and the Latimer Clark has been kindly tested for me by Professor Ayrton against his standard. Its E.M.F. at 10° C. is 1·433 volts (the temperature at which the experiments were made). Commercial cadmium and polished electro-cadmium were used. They gave the same deflection on the electrometer.

The method employed was to make up various solutions containing varying amounts of cadmium iodide and free iodine, and then place them in the cell and measure the E.M.F. produced. In this way we measure the E.M.F. produced by the combination of an infinitely small quantity of cadmium and iodine under definite conditions, and so determine a point on one of our curves.

A very brief description of each group of experiments will be sufficient after the above explanation.

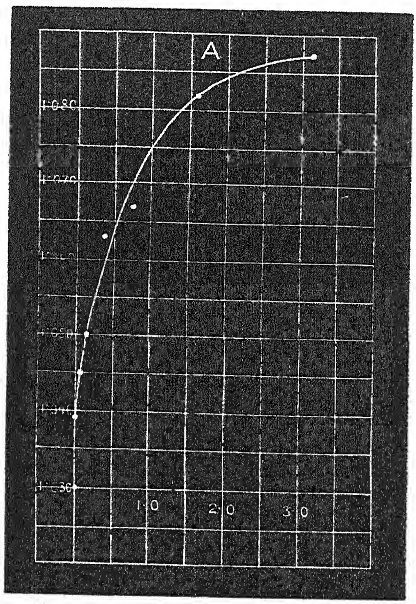
Firstly, I tested the effect of diminishing the amount of free iodine present, the cadmium iodide in solution remaining the same. The results are given in curve and Table A. The experiments were not made so carefully as those that follow, but are sufficient to show that the E.M.F. is a continuous function of the free iodine present, and

that the curve flattens off as we approach saturation with iodine as we should expect. There is no indication of a compound.

TABLE A.

E.M.F. of cadmium cells.	Grams of free iodine in 1 c.c. of a 1 per cent. cadmium iodide solution.
1·087	0·0032
1·081	0·0016
1·067	0·0008
1·063 (?)	0·0004
1·050	0·0002
1·045	0·0001
1·039	0·00005

E.M.F. of cadmium cell.



Milligrams of free iodine in 1 c.c. of solution.

Secondly, I tested the effect on the E.M.F. of the cell of increasing the amount of the cadmium iodide present. Each solution was saturated with iodine with the view of having the iodine free to combine with the cadmium in each case, so that I could measure the changes in the difference of potential between the cadmium iodide and the water alone. The results are given in curve and Table B. There is no indication of a compound between the cadmium iodide and the

water, but the curve is continuous, flattening as we approach saturation.

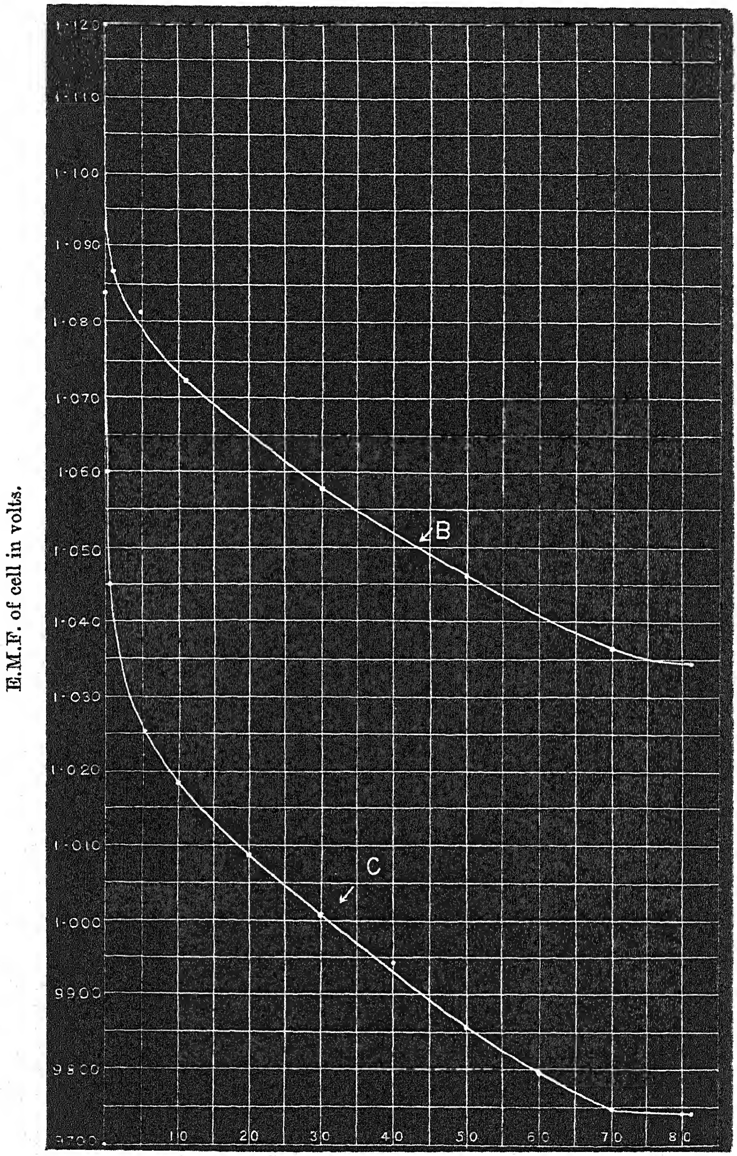
TABLE B.

E.M.F. of cadmium cells.	Grams of cadmium iodide in 100 grams of water.	Grams of free iodine in 1 c.c. of the solution.
1·119	0·1	0·0008
1·087	1·0	0·0032
1·081	5·0	0·0071
1·072	11·4	0·0095
1·057	30·0	0·0113
1·046	50·0	0·0151
1·036	70·0	0·0202
1·034	81 sat. at 10° C.	0·0300

Thirdly, I tested the effect of increasing the amount of cadmium iodide present, keeping the amount of iodine present constant. The results are given in curve and Table C. Here we have two effects, one superposed on the other. Firstly, the gradual diminution of the difference of potential between the cadmium iodide and the water, which is shown by curve B. Secondly, the diminution in the difference of potential between the cadmium and the iodine, due to the effect on the iodine of the increasing amount of cadmium iodide in solution. Evidently any number of curves, starting from different points along curve B and lying below it, could be drawn for different constant amounts of free iodine present. These experimental results then bear out the description of the probable variations in E.M.F. given at the beginning of the paper.

TABLE C.

E.M.F. of cadmium cells.	Grams of cadmium iodide in 100 grams of water.
1·084	0·1
1·060	0·49
1·045	1·1
1·025	5·1
1·018	0·0
1·008	20·0
1·001	30·0
0·994	40·0
0·985	50·0
0·980	60·0
0·975	70·0
0·974	80·0
0·974	81·0



Grams of salt in 100 grams of water.

We have next to consider the effect of change of temperature on the electromotive force of the cell. The importance of such measurements has been sufficiently explained in my Zinc-Iodine paper, where I

have given an account of Professor Helmholtz's work on this subject. It is sufficient to state here that we can obtain a measure of the difference between the electrical energy produced during a reaction, and the whole heat set free by the reaction, if we measure the variations in E.M.F. caused by variations in temperature.

The calculation is made by means of the following formula :—

$$T\frac{de}{dt} = J \, . \, dQ,$$

where de is the variation of E.M.F. caused by altering the absorbed temperature T by the amount dt; and dQ is the difference between the electrical energy and the heat produced by the reaction. I have then, applying this formula, made some experiments to settle the following question. When a salt is dissolved in water, the heat set free or absorbed is made up of two parts, the heat of solution of the salt in water, and the latent heat of liquefaction of the salt. It is usually assumed that when a salt is *formed* in presence of water, as in the combination of cadmium and iodine, that this latent heat enters into the thermal result, that the salt is formed in the *solid* state and then dissolved : I have obtained some evidence that the salt is formed in the liquid state. Iodide of zinc sets free heat on dissolving in water. Iodide of cadmium absorbs heat on dissolving in water. Nevertheless, both salts give similar curves as representing their E.M.F. of solution in water. This naturally suggests the question whether the latent heat of liquefaction enters into the energy set free when the salt is *formed* in presence of water, or to put it in another way, whether the salt is *formed in the solid* or *formed in the liquid state*, when the metal and iodine combine.

If, as I suppose, the salt is formed in the liquid state, and the latent heat of liquefaction does not enter into the energy set free during the reaction, we should expect that in a cell in which solid salt was separated by the passage of the current, there would be a considerable rise of E.M.F. due to the heat set free by the passage of the salt, when formed, from the liquid to the solid state. If there was no rise in E.M.F., and the curves B and C show that there is none, then we should have to suppose that this latent heat appeared as heat in the cell.

This then is a point for experiment by the application of the above formula. I have found the measurement of temperature effect very troublesome, as the iodine rapidly attacks the cadmium at high temperatures, and have had therefore to use a cadmium-silver iodide cell. This consists of a cadmium plate and silver wire coated with silver iodide, immersed in a cadmium iodide solution. I have used five or six cells in series, placed inside an ordinary hot water oven. I first

experimented on cells containing dilute cadmium iodide. This cell showed no variation on the electrometer on being raised through 40° C., showing that its E.M.F. does not vary 0·00002 volt per degree Cent. I next experimented on cells containing saturated solution of cadmium iodide. I detected a slight diminution in E.M.F. on raising them through 40° C., but not enough for measurement. These two sets of experiments may be taken as showing that practically the whole of the energy set free by the reaction between cadmium and iodine appears as electrical energy. Thirdly, I experimented on cells containing a large excess of solid salt, so that the solution should be saturated throughout the whole range of temperature, and consequently the passage of a current would separate solid cadmium iodide. I immediately obtained a very considerable diminution of E.M.F. on warming the cell. I found it impossible to measure it accurately, as for various reasons both the E.M.F. of the cells and the temperature effect kept varying.

A very laborious series of experiments ultimately enabled me to detect the causes of these fluctuations, but not to remedy them with the apparatus at my disposal. I therefore only give a rough approximation to this temperature effect at present. It is about 0·00037 volt per degree C. This means that in a cell in which the passage of the current causes the separation of *solid* salt there is set free about 4000 heat-units for every gram-molecule of cadmium iodide. The value of the electrical energy set free in heat-units by the formation of the solution $CdI_2,400H_2O$, is about 2000 heat-units. Consequently, if the theory described above is correct, we should expect an absorption of heat of about 2000 heat-units on dissolving cadmium iodide in water ($CdI_2,400H_2O$). This result is much too high, as Thomsen gives the value 1000 heat-units as the amount of heat absorbed. As already explained, the value given for the temperature effect is a very rough approximation, so that I think this result, as far as it goes, distinctly supports the above explained theory that when a salt is *formed* in presence of water, the latent heat of liquefaction does not enter into the energy set free.

Before concluding this paper I wish to draw attention to a point of some interest. On looking at curve B or C, it is obvious that a trace of salt, as little as 0·1 per cent., has a marked effect on the E.M.F. of the cell. This can hardly be explained on the usual theory of molecular compounds, unless we are prepared to write as one molecule $CdI_2,20000H_2O$. Some other explanation must be found, but whatever this may be, the result is noteworthy as showing the enormous distance, compared to its molecular diameter, to which the molecule is able to influence the difference of potential between the water and the next molecule of salt which is going to dissolve.

Whether or no there is any limit to this can only be decided by experiments made with water prepared with the utmost care. Ordinary distilled water cannot be considered as sufficiently pure, but on trying it I obtained an E.M.F. higher than any given on Table B.

There is another subject on which the curves probably have an important bearing, namely, partial double decomposition between two salts in solution, but I have not yet sufficient experimental evidence to justify me in explaining their importance in this direction. In conclusion, I must explain that all experimental details have been omitted from this paper, but will probably be published elsewhere.

LXVI.—*Contributions to our Knowledge of the Chlorid[illegible]mony.*

By RICHARD ANSCHÜTZ and P. [illegible]N EVANS.

IN the course of a research on the action of anhydrous oxalic acid on inorganic chlorides, we have made an observation with reference to antimony pentachloride that appears to us remarkable.

We prepared pure antimony pentachloride by the action of chlorine on antimony trichloride. To assure ourselves of the purity of the trichloride it was distilled under diminished pressure, and was found to boil constantly at 113·5° under 23 mm., and at 103° under 14 mm. pressure.

The pure antimony trichloride was supersaturated with chlorine and the liquid product then distilled under diminished pressure to purify it.

Trial I.—19·15 grams of $SbCl_3$ after saturation with chlorine gave 26·45 grams crude product, this after distillation gave 24·65 grams of $SbCl_5$ instead of 25 grams reckoned.

Trial II.—126·5 grams of $SbCl_3$ after saturation with chlorine gave 174·5 grams crude product, this after distillation gave 163·1 grams of $SbCl_5$ instead of 166·1 grams reckoned.

These figures show that *antimony pentachloride boils without sensible decomposition under diminished pressure*, and this was further confirmed by two determinations of the chlorine.

I. 0·2419 gram $SbCl_5$ gave 0·5796 gram AgCl.
II. 0·1720 ,, ,, 0·4120 ,,

	Calculated for $SbCl_5$.	Found. I.	Found. II.
Cl....	59·24	59·28	59·26

It is interesting that the boiling point of antimony pentachloride lies considerably lower than the boiling point of the trichloride under the same pressure: thus, under 22 mm. it boils constantly at 79°, and under 14 mm. at 68°.

As in the literature of the subject we can find no details of the dissociation of antimony pentachloride, we have resolved to occupy ourselves with a study of this question. We reserve a discussion as to whether indeed antimony pentachloride boils under a low pressure without decomposition, until we shall have made a vapour-density determination under much diminished pressure. Should there be no true boiling under our conditions of pressure but rather dissociation, it is remarkable that antimony trichloride should exist as a gas in the gaseous mixture, at a temperature which is considerably under its own boiling point at the same pressure.

Bonn University, July, 1886.

LXVII.—*Pipitzahoic Acid.* (First Communication.)

By Richard Anschütz and John Walter Leather.

In the year 1855 Weld (*Annalen*, **95**, 188) published a paper entitled "Ueber die Pipitzahoïnsaeure, einen eigenthümlichen Pflanzenstoff," describing an acid substance which Professor Rio de la Loza had extracted from the roots "raïz del pipitzahuac" and had called "pipitzahoïnsaeure." Liebig received a small quantity of this pipitzahoïnsaeure (pipitzahoic acid) from Dr. Schaffner, a German physician, of San Luis Potosi (Mexico), and gave it to Weld for investigation. In 1856 Schaffner discovered the plant itself and gave it the name *Trixis pipitzahuac*. Specimens of the plant and large quantities of the dried roots, together with a large quantity of other Mexican plants formerly the property of the late Dr. Schaffner, came into the hands of his friend Mr. Vigener, apothecary in Biebrich on the Rhine.

Vigener again drew the attention of the scientific world to the raïz del pipitzahuac, which in Mexico is highly valued medicinally, the inhabitants using it as an energetic purgative, its application being unaccompanied with disagreeable results. On March 3, 1884, Vigener (*Sitzungsber. d. niederrhein. Gesellschaft in Bonn*, 1884, 86) laid samples of pipitzahoic acid before a meeting of the Niederrheinische

Gesellschaft für Natur- und Heilkunde in Bonn, declaring it to be an anthraquinone-derivative, and suggested that one of us (Anschütz) should submit it to a chemical investigation, a proposition which was accepted with pleasure. The reactions of pipitzahoic acid which were then observed by one of us (Anschütz) (*ibid.*, 1884, 145), led him to form an opinion of the constitution of this acid which has not been altered by any of our later experiments.

With regard to the anatomical structure of the plant from which pipitzahoic acid is derived, there is probably scarcely a substance which is so clearly seen on superficial examination as pipitzahoic acid, as it is contained only in the pipitzahuac roots and is distinguished by its golden-yellow colour. At our request Professor Schimper had the kindness to examine the roots, and we take this opportunity of rendering him our best thanks for the following communication:—

"The yellow crystalline substance of the root of *Trixis pipitzahuac* is contained in large, cylindrical, intercellular passages which are limited to the sieve tubes of the fibro-vascular bundles, three or four occurring in each of the bundles. In the remaining parts not a trace of this substance can be recognised even with the highest power of the microscope.

"From the mode of its appearance it may be assumed as extremely likely that pipitzahoic acid represents a product of metastasis which is of no further use in the plant, similarly to the ethereal oils in the resin-canals of the Umbelliferæ. Similar receptacles occur among the representatives of the Composites to which the *Trixis pipitzahuac* belongs, and it is probable that the contents of such receptacles have in all cases the same physiological value.

"A similarity in the manner of its appearance with that of the colouring matter of the madder-root (*Rubia tinctorium*) does not exist. Alizarin (more properly its chromogen) is not confined to special receptacles, but is contained in all parenchymatic cells, especially those of the bark.

"The root of *Trixis pipitzahuac* is somewhat rich in glucose, its parenchyma contains colourless, sharp-edged bodies which are slightly optically active, but do not appear to me to be crystalline. The small intercellular spaces around the fibres, which are dispersed in small groups in the bark and the pith, are filled with a brown solid substance.

"Substances other than those above-mentioned could not be distinguished by the aid of the microscope."

The appearance of pipitzahoic acid suggested that this substance might be included in the group of the quinones. Regarding in the light of our present knowledge the facts discovered by Weld years ago, more especially the property of forming alkaline salts which

are decomposable by carbonic anhydride and dissolve in water with a beautiful violet-red colour, it appeared probable that pipitzahoic acid is a hydroxyquinone, and the comparison of pipitzahoic acid with alizarin was also thereby suggested: but a little consideration showed that pipitzahoic acid cannot belong to the group of the hydroxy-anthraquinones, especially as the form in which it appears in *Trixis pipitzahuac* is quite different from that of alizarin in *Rubia tinctorium*.

Taking into account both Weld's observations and experiments of his own which had served to determine the quinone-like character of pipitzahoic acid, and the formula also $C_{15}H_{20}O_3$ (with old atomic weights $C_{30}H_{20}O_6$), one of us (Anschütz, *Ber.*, **18**, 709) published some time ago the following considerations as to its constitution.

"If from the formula of pipitzahoic acid the formula of monhydroxy-quinone be subtracted, there is a difference of $C_9H_{16} = C_{15}H_{20}O_3 - C_6H_4O_3$. Now supposing that in hydroxyquinone one of the three benzene hydrogen-atoms is displaced by a single hydrocarbon-group, this side-chain must be C_9H_{17}, but the group C_9H_{17} contains so many hydrogen-atoms that only two of the nine carbon-atoms can be doubly linked, and therefore a second benzene-ring cannot be present in pipitzahoic acid. In hydroxybenzoquinone there are, however, three benzene hydrogen-atoms which it is possible may be displaced by hydrocarbon-groups; in other words, it is conceivable that in pipitzahoic acid either one hydrogen-atom is displaced by C_9H_{17}, or that two are displaced by C_9H_{18}, or three by C_9H_{19}. The group C_9H_{17} is a radicle of a hydrocarbon of the C_nH_{2n+1} series. If two hydrogen-atoms are displaced by distinct radicles which in sum are equal to C_9H_{18}, one of these must be a C_nH_{2n+1} and the other a C_nH_{2n-1} radicle, and in like manner if three radicles are present two must belong to the C_nH_{2n+1}, and one to the C_nH_{2n-1} series. In short, whether one, two, or three of the hydrogen-atoms in the hydroxy-quinone be displaced by hydrocarbon radicles, one side-chain in pipitzahoic acid will contain a pair of doubly-linked carbon-atoms."

Hence arises the question, how many and what side-chains does the monohydroxybenzoquinone present in pipitzahoic acid contain? It may be fitting at once to mention here that we have so far only succeeded in answering the first part of the question, and in showing by means of an indirect method that pipitzahoic acid most probably contains two side-chains.

Before proceeding to the description of our investigations, we must point out that several months after the publication of the paper which one of us read on pipitzahoic acid, on August 4, 1884, at a meeting of the Niederrheinische Gesellschaft für Natur- und Heilkunde in Bonn, a paper was published by Mylius (*Ber.*, **18**,

480) on the same subject, and a short time afterwards a second communication (*ibid.*, 18, 936) followed by the same author. We shall take the opportunity at different points in this paper of comparing our results with those obtained by Mylius. We do not agree with this author's proposal to give pipitzahoic acid the name *perezone*, for it appears to us of little purpose to exchange the already well-known name pipitzahoic acid (pipitzahoïnsaeure) for a name which gives us just as little idea of the constitution of the substance as the old one. When the structure of pipitzahoic acid has been fully made out, a more rational name will suggest itself without any difficulty.

1. *Preparation of Pipitzahoic Acid.*

For 50 grams of nearly pure pipitzahoic acid, one of us is indebted to Mr. Vigener; we obtained the remainder of that which we used—somewhat over 200 grams—by extraction from 6 kilos. of *Radix pereziæ*. The roots were pulverised as finely as possible and boiled for half an hour with 10 times their weight of alcohol on the water-bath. The solution poured off from the insoluble residue was filtered and about nine-tenths of the alcohol distilled off. On pouring this concentrated solution into about five or six times its volume of water at 50° C., a golden-yellow, crystalline precipitate of pipitzahoic acid was produced. The filtrate from this precipitate is light brown coloured; in thin layers it is nearly transparent, but no precipitate is discernible even with the help of a pocket lens. By extracting with ether and evaporating the solution, or by evaporating the filtrate itself under the air-pump or on the water-bath, considerable quantities of a dark brown, tarry product are obtained which we did not submit to any further examination.

The residue after extraction with alcohol still contains a considerable quantity of pipitzahoic acid, and must be again treated twice in the above-mentioned way; in our experiments the third extract contained only very small quantities of the acid.

Three portions of roots were treated with the following results:—

200 grams	roots gave	10·8 grams	pipitzahoic acid	= 3·6	per cent.
1600 grams	,,	55·7 grams	,,	= 3·5	,,
4000 grams	,,	147·0 grams	,,	= 3·7	,,

The dried crystalline precipitate melted at 100°, whereas pure pipitzahoic acid melts at 103—104°. Mylius gives 106—107°. The pipitzahoic acid was not further purified for the preparation of the various derivatives.

Pure pipitzahoic acid may be easily obtained by crystallisation from dilute alcohol or benzene, and then consists of beautiful, golden-yellow,

flat plates. It is rather difficultly combustible; burnt with lead chromate—

(1.) 0·1850 gave 0·4870 CO_2 and 0·1384 H_2O.

On combustion with lead chromate—

(2.) 0·1773 gave 0·4673 CO_2 and 0·1329 H_2O.

Burnt with copper oxide in a current of oxygen—

(3.)	0·2184	gave	0·5760	CO_2 and	0·1588	H_2O.
(4.)	0·2102	,,	0·5549	,,	0·1500	,,
(5.)	0·1963	,,	0·5181	,,	0·1443	,,
(6.)	0·1960	,,	0·5208	,,	0·1456	,,
(7.)	0·1421	,,	0·3768	,,	0·1048	,,

	Calculated for $C_{15}H_{20}O_3$.	Found.						
		I.	II.	III.	IV.	V.	VI.	VII.
C....	72·58	71·79	71·88	71·94	72·00	72·03	72·47	72·37
H...	8·06	8·31	8·33	8·08	7·93	8·16	8·26	8·19

Pipitzahoic acid sublimes easily; it distils with steam, but it is decomposed by protracted boiling with water. It dissolves readily in alcohol, ether, chloroform, glacial acetic acid and benzene; it is also somewhat soluble in light petroleum. Hot glacial acetic acid appears to decompose it.

2. *Salts of Pipitzahoic Acid.*

Weld has examined several salts of pipitzahoic acid. He has also drawn attention to the characteristic colour of their solutions, which is like that of potassium permanganate. He found that the barium, calcium, sodium and lead salts are decomposed by carbonic anhydride. Weld also analysed the copper and silver salts. We endeavoured to prepare the potassium and silver salts in order to obtain ethers of pipitzahoic acid: we could only obtain the potassium salt in the form of a black tarry mass, but were more successful in preparing the silver salt by adding silver nitrate in excess to an aqueous solution of the potassium salt, whereby the violet-brown precipitate which Weld describes was formed. But this precipitate was very difficult to filter, remaining in a frothy condition, even after shaking, and is therefore very difficult to obtain in a pure state. After washing with water, in which it is insoluble, and drying in a vacuum desiccator, the silver salt forms a purplish-blue, amorphous powder, which is easily soluble in alcohol, very slightly soluble in water, and insoluble in ether. Analysis gave the following result:—

0·2000 silver salt gave 0·0600 silver.

	Calculated for $C_{15}H_{19}O_3Ag$.	Found.
Ag	30·42	30·00

3. *Attempt to Prepare an Ethyl Ether of Pipitzahoic Acid.*

As ethyl iodide gave tarry products with the silver salt we used ethyl bromide. After heating the silver salt with five times its weight of ethyl bromide in a closed tube for one hour in the water-bath, considerable pressure was observed on opening the tube. The liquid portion, after filtering from silver bromide, was freed from excess of ethyl bromide by distillation or spontaneous evaporation, and a dark red liquid then remained from which a very small amount of a crystalline substance gradually separated; this substance crystallised from alcohol in white prisms, melting at 141° C. We did not obtain sufficient for a combustion.

4. *Attempt to prepare an Acetic Ether of Pipitzahoic Acid.*

The acid was heated with three times its weight of acetic anhydride for three days in a sealed tube in the water-bath. The completion of the reaction is easily determined, for not only does the colour of the liquid become lighter, but whilst at first on cooling the tube pipitzahoic acid crystallises out, this is not the case when the reaction nears completion. On evaporating the contents of the tube over soda-lime, the product of the reaction separates in large, colourless crystals, which may be purified by recrystallisation from alcohol. The compound thus prepared forms well-characterised prisms; it melts at 115° C., and is easily soluble in alcohol, ether, chloroform and glacial acetic acid.

Dr. Hintze was kind enough to examine the crystals, and communicated the following description to us:—

"*System: orthorhombic.*

Ratio of the axes $a : b : c :$ = 0·62933 : 1 : 0·84507

Observed faces: c = (001)0P
p = (110)∞P
m = (120)∞P̆2
d = (011)P̆∞
q = (012)½P̆∞.

Angles of the Normals.

	Calculated.	Found.
001 : 011 =	—	40° 12′
001 : 012 =	22° 54′	22 48
011 : 012 =	17 18	17 24
110 : 1$\bar{1}$0 =	64 22	64 20
110 : 120 =	19 21	19 23
120 : 1$\bar{2}$0 =	103 4	102 48
110 : 011 =	—	69 52
120 : 012 =	59 39	60 0

"The crystals are of a short prismatic habit; the vertical faces are distinctly striated."

It is noteworthy that the compound is white, whereas the ethers of the hydroxyquinones and the quinones themselves are generally coloured. Its behaviour with caustic potash is also remarkable: the acid ethers of the hydroxyquinones are easily decomposed by this reagent, the hydroxyquinone being regenerated, whereas the product of the action of acetic anhydride on pipitzahoic acid appears to remain unchanged on treatment with caustic potash, for the substance thus obtained melted at 113°, and the violet-blue colour of the potassium salt of pipitzahoic acid did not make its appearance. Since the decomposition of this compound, melting at 115° C., into pipitzahoic acid and acetic acid did not succeed, we cannot with certainty maintain that we have obtained the acetic ether of pipitzahoic acid, notwithstanding that the results of analysis agree very well with the formula of a monacetate: thus

(1.) 0·1523 gave 0·3909 CO_2 and 0·1105 H_2O.
(2.) 0·1024 ,, 0·2645 ,, 0·0700 ,,
(3.) 0·1454 ,, 0·3739 ,, 0·1004 ,,

	Calculated for $C_{15}H_{19}O_3 \cdot C_2H_3O$.	Found. I.	II.	III.
C	70·35	70·00	70·44	70·13
H	7·58	8·06	7·59	7·67

5. *Attempt to reduce Pipitzahoic Acid.*

(*a.*) *By Stannous Chloride.*—A solution of pipitzahoic acid may be decolorised by the action of sulphurous acid, or zinc-dust and acetic acid, or stannous chloride and hydrochloric acid, a compound being formed which is exceedingly soluble in water. We gave stannous chloride the preference because the tin can be easily and completely removed by means of sulphuretted hydrogen. An alcoholic solution

of pipitzahoic acid was poured into a solution of stannous chloride in hydrochloric acid, and the tin precipitated by sulphuretted hydrogen gas from the colourless solution heated to about 50°. The sulphides of tin were filtered off as rapidly as possible, and the clear colourless solution thus obtained was concentrated in a stream of carbonic anhydride on the water-bath under a pressure of about 40 mm. During this operation we noticed that when the solution became somewhat concentrated, almost colourless oily drops commenced separating; that as the distillation proceeded these became yellow, then brown, and lastly, when almost all the water had gone over, they remained as a tar at the bottom of the flask.

Exactly similar results were obtained on using sulphurous acid.

The tar obtained by the decomposition of the reduced pipitzahoic acid recalls in some respects the tar remaining after the evaporation of the brown filtrate obtained in the preparation of pipitzahoic acid from *Radix pereziæ*. If air be passed through an aqueous solution of the reduced pipitzahoic acid, the liquid becomes yellow, and the quinone is rapidly precipitated. Further attempts to isolate the hydroquinone, which is apparently very unstable, were given up, the more so because other experiments removed all doubt of the quinone-like character of pipitzahoic acid.

(*b*.) *Distillation of Pipitzahoic Acid over Zinc-dust.*—One gram of pipitzahoic acid was intimately mixed with 20 grams of zinc-dust, filled into a hard glass combustion-tube, another 20 grams of zinc-dust filled in in front, and distilled in a current of hydrogen at a low red heat. Twenty such operations produced 5 grams of a dark red oil, which, on distillation, passed over at from 50° to 330° C., no portion exhibiting a more constant boiling point than another. As much larger quantities of the acid must have been used to secure a definite result, we have for the present postponed the repetition of this experiment.

6. *Action of Sulphuric Acid on Pipitzahoic Acid.*

On treatment either with concentrated or with dilute (1 vol. : 1 vol.) sulphuric acid, pipitzahoic acid appears to char at once. No more satisfactory result was obtained when the sulphuric acid was diluted with acetic acid. On the other hand, hydroxypipitzahoic acid, which is described later on, reacts very easily with sulphuric acid on warming, as Mylius found, whereby a yellow substance, named by him "perezinone," which contains the elements of one molecule of water less than hydroxypipitzahoic acid, is formed. We have also made the experiment, and can corroborate Mylius's results.

Action of Bases on Pipitzahoic Acid.

During the past few years various authors, especially Zincke, V. Meyer, and Goldschmidt, have shown that the quinones behave in a characteristic manner when submitted to the action of amines, of phenylhydrazine, and of hydroxylamine. In order to prove, therefore, the quinone-like nature of pipitzahoic acid, we have subjected it to the action of these bases, and have found that it very readily reacts with the amines, in the same way as do the quinones of the benzene series.

1. *Amine-derivatives of Pipitzahoic Acid.*

The investigations of Zincke and several of his pupils have shown that the benzoquinones react with primary and secondary amines generally in such a way that one molecule of the quinone withdraws from another molecule one atom of hydrogen, and a second atom of hydrogen from the amine. The one molecule of the quinone thus becomes reduced, and the residue of the second molecule combines with the amine-group. This reaction may be repeated with the alkylated or phenylated monamidoquinone, and an alkylated or phenylated diamidoquinone formed. Sometimes this reaction is accompanied by another chemical change, which consists in one of the quinone oxygen-atoms being displaced by an amido-group, the oxygen combining with the two hydrogen-atoms of the amine to form a molecule of water; this is the case, for instance, in the formation of dianilidobenzoquinone anilide.

The compounds formed by these reactions are generally solid crystalline substances of a dark blue, violet-blue, or red colour. They are prepared by adding a primary or secondary amine to a solution of a quinone in alcohol or glacial acetic acid. Even in the cold the liquid becomes dark coloured, and if the solution be not too dilute, the newly-formed substance crystallises out after a short time. If these substituted amidoquinones are boiled with dilute sulphuric acid or hydrochloric acid in alcoholic solution, each of the amine-groups is displaced by hydroxyl, the amine being reproduced. This last-mentioned reaction affords an excellent method for the preparation of the hydroxyquinones, and offers at the same time a possibility of determining the number of the amine-groups which have been introduced. On account of these facts we investigated the action of aniline, orthotoluidine and paratoluidine on pipitzahoic acid.

(*a.*) *Anilidopipitzahoic Acid*, $C_{15}H_{18}\begin{cases} O_2 \\ OH \\ NH{\cdot}C_6H_5 \end{cases}$.—To prepare this compound excess of aniline is added to an alcoholic or acetic acid

solution of pipitzahoic acid. At first the liquid turns violet-red, and if sufficiently concentrated becomes thick on standing, owing to the separation of crystals, which consist of small violet prisms. If these crystals are filtered off and the mother-liquor be allowed to stand exposed to the air, the hydroquinone of pipitzahoic acid formed in the reaction becomes oxidised, and the pipitzahoic acid thus regenerated reacts in the same way with the excess of aniline. We thus obtained 12·5 grams of anilidopipitzahoic acid from 10 grams of pipitzahoic acid, whereas, according to theory, we ought to have obtained 13·6 grams. The formation of the anilide takes place in accordance with the following equation:—

$$2C_{15}H_{19}(O_2)\cdot OH + NH_2\cdot C_6H_5 = C_{15}H_{18}\begin{cases} O_2 \\ OH \\ NH\cdot C_6H_5 \end{cases} + C_{15}H_{19}(OH)_3.$$

Anilidopipitzahoic acid forms dark purple, shining needles, which melt at 133° C. In alcohol, ether, benzene, chloroform, and acetic acid, it is easily soluble, and may be crystallised from warm alcohol or acetic acid. Analysis gave the following results:—

(1.) 0·3097, burnt with powdered CuO, gave 0·8406 CO_2 and 0·2181 H_2O.
(2.) 0·2524, burnt with powdered CuO, gave 0·6829 CO_2 and 0·1756 H_2O.
(3.) 0·2277, burnt in open tube with oxygen, gave 0·6178 CO_2 and 0·1581 H_2O.
(4.) 0·1974, burnt in open tube with oxygen, gave 0·5356 CO_2 and 0·1362 H_2O.
(5.) 0·4952 gave 18·6 c.c. N at 25° C., under 763·1 mm.

	Calculated for $C_{21}H_{25}O_3N$.	Found. I.	II.	III.	IV.	V.
C	74·34	74·03	73·77	74·00	74·00	—
H	7·37	7·81	7·72	7·71	7·66	—
N	4·13	—	—	—	—	4·18

(*b.*) *Orthotoluidopipitzahoic Acid*, $C_{15}H_{18}\begin{cases} O_2 \\ OH \\ NH[2]C_6H_4[1]CH_3 \end{cases}$, is prepared from orthotoluidine and pipitzahoic acid in the same way as anilidopipitzahoic acid, although a good yield may more easily be obtained by making use of an alcoholic solution. 5 grams of pipitzahoic acid gave 5 grams of toluide instead of 7·1 grams. Orthotoluidopipitzahoic acid crystallises from warm alcohol in needles which melt at 109—111° C. Mylius observed the melting point 135—136° C. How this difference is caused we are unable to state. Orthotoluido-

pipitzahoic acid does not show any metallic lustre; it is easily soluble in alcohol, ether, benzene, chloroform and acetic acid. Analysis gave the following results:—

(1.) 0·2059 substance gave 0·5620 CO_2 and 0·1475 H_2O.
(2.) 0·4587 ,, ,, 16·7 c.c. N. at 11° C. and 752 mm.

	Calculated for $C_{22}H_{27}O_3N$.	Found. I.	II.
C..........	74·79	74·45	—
H..........	7·65	7·96	—
N..........	3·96	—	4·34

(*c.*) *Paratoluidopipitzahoic Acid*, $C_{15}H_{18}\begin{cases} O_2 \\ OH \\ NH[4]C_6H_4[1]CH_3 \end{cases}$, is prepared in the same manner as anilido- and orthotoluido-pipitzahoic acid. This paratoluide, after having been several times recrystallised from alcohol, forms long, blue needles, without metallic lustre, melting at 136° C. It is easily soluble in ether, alcohol, benzene, chloroform and acetic acid. Analysis gave the following results:—

(1.) 0·2478 substance, burnt with $PbCrO_4$, gave 0·6689 CO_2 and 0·1809 H_2O.
(2.) 0·2187 substance, burnt with $PbCrO_4$, gave 0·5914 CO_2 and 0·1589 H_2O.
(3.) 0·2341, burnt in a current of oxygen, gave 0·6417 CO_2 and 0·1688 H_2O.
(4.) 0·4416 gave 15·8 c.c. N at 19° C., and 756 mm.

	Calculated for $C_{22}H_{27}O_3N$.	Found. I.	II.	III.	V.
C......	74·79	73·62	73·75	74·75	—
H......	7·65	8·11	8·07	8·01	—
N......	3·96	—	—	—	4·14

Anilido-, orthotoluido- and paratoluido-pipitzahoic acids behave with reagents as follows:—On treatment with stannous chloride dissolved in hydrochloric acid, or zinc-dust and acetic acid, their solutions are decolorised, but on exposure to the air the original compound is reproduced, and hence it would appear that the quinone oxygen-atoms remain intact in these three derivatives. Anilido- and the two toluido-pipitzahoic acids dissolve in concentrated sulphuric acid with a blue colour; if these solutions be poured into a large quantity of water no precipitates are formed, but simply a purple-red liquid. The three acids dissolve with difficulty in alkaline solutions. The concentrated solutions in alkalis are of a violet-red colour, which, on the addition

of much water, passes into green. By heating with ammonia in a closed tube the aniline and toluidine groups become displaced by the amido-group. It is noteworthy that we have obtained in these three derivatives no substances which may be looked upon as diamine-derivatives, and from this it may be inferred that there is only one benzene hydrogen-atom in pipitzahoic acid.

(*d.*) *Amidopipitzahoic Acid*, $C_{15}H_{18}\begin{cases}O_2\\OH\\NH_2\end{cases}$.—If the anilide or the toluides of pipitzahoic acid are boiled with ammonia they suffer a change, their violet-blue colour passing into red-brown. In order to prevent the escape of ammonia these operations were carried out in sealed tubes. On account, however, of the fact that even after six hours' heating at 100° C., considerable quantities of undissolved substance remained in the tubes, we used alcoholic ammonia and heated as before for six hours in the water-bath. In each case the violet-blue colour of the solutions changed to blue.

The tubes in which we had used aqueous ammonia contained blue liquids, and also insoluble substances, consisting of dark-brown crystals contaminated with some tar. On concentrating the blue filtrates large quantities of dark brownish-red, shining crystals separated, and the blue colour of the solutions changed to brown. The brown crystals from the tubes, mechanically separated from the tar, melted at 135—140° C., the crystals from the mother-liquors at 146—149°, whether the material used had been the anilide or either of the toluides of pipitzahoic acid. All the products consist of the same substance in different degrees of purity. We did not, however, further investigate the action of aqueous ammonia, as we obtained the same compound by the use of alcoholic ammonia, in which latter case no tar was produced. On evaporation of the alcoholic solutions, the smell of aniline or ortho- or para-toluidine could easily be detected. In order to determine the quantity of the amine which was in each case set free, we subjected to distillation with steam the three blue solutions obtained by heating with alcoholic ammonia. Shortly after the commencement of the distillation, the blue colour of the solutions changed to brown, and large quantities of dark reddish-brown crystals were precipitated which melted at 150° C., and consisted of amidopipitzahoic acid.

Four grams of anilide was heated for six hours at 100° C. with about three times the theoretical quantity of concentrated alcoholic ammonia. The contents of the tubes was then distilled with steam, and the distillate containing ammonia and aniline was extracted three times with ether. This ethereal extract was washed with water until it no longer turned litmus-paper blue; an excess of hydrochloric acid

was then added, and the solution evaporated to dryness on the water-bath. The residue consisted of nearly pure aniline hydrochloride, and weighed 1·2 gram, whereas according to the equation—

$$C_{15}H_{18}\begin{cases} O_2 \\ OH \\ NHC_6H_5 \end{cases} + NH_3 = C_{15}H_{18}\begin{cases} O_2 \\ OH \\ NH_2 \end{cases} + C_6H_5NH_2,$$

we ought to have obtained 1·5 grams of aniline hydrochloride.

Operating in the same way we obtained from 2·1 grams of para-toluidopipitzahoic acid, 0·7 gram of paratoluidine hydrochloride instead of 0·85 gram, and 1·45 grams amidopipitzahoic acid instead of 2·1 grams.

When crystallised from alcohol, amidopipitzahoic acid forms reddish-brown, shining crystals which melt at 151° C. It dissolves in solutions of the alkalis and ammonia with a deep blue colour, which is not changed on addition of water. On boiling with water the ammonia salt is decomposed, amidopipitzahoic acid is precipitated, and the blue colour of the solution disappears. Amidopipitzahoic acid is insoluble in water, but is easily soluble in alcohol and ether. Subjected to reducing agents such as stannous chloride and hydrochloric acid it dissolves easily, the solution being decolorised. If these colourless reduced solutions are exposed to the air, or if air is injected into them, the hydro-compounds are oxidised and amidopipitzahoic acid is precipitated. It dissolves in cold concentrated sulphuric acid forming a reddish-brown solution, which becomes red on addition of much water. On boiling with dilute sulphuric acid, amidopipitzahoic acid is converted into hydroxypipitzahoic acid. Analysis gave the following results:—

(1.) 0·1493 substance gave 0·3713 CO_2 and 0·1128 H_2O.
(2.) 0·3124 „ 16·2 c.c. N at 20° and 753 mm.
(3.) 0·4175 „ 19·5 „ 13° „ 752 „

	Calculated for $C_{15}H_{21}NO_3$.	Found. I.	II.	III.
C........	68·44	67·83	—	—
H	7·98	8·38	—	—
N	5·33	—	5·95	5·55

(*e.*) *Proof of the Identity of Mylius's "Perezonoxime" with Amidopipitzahoic Acid.*—In order to characterise pipitzahoic acid as a quinone Mylius treated it with hydroxylamine. According to Goldschmidt the benzoquinones are only reduced to hydroquinones by the action of hydroxylamine, whereas by the action of hydroxylamine hydrochloride paranitrosophenols are formed (quinone-oximes). [It is still

doubtful whether the nitrosophenols are properly regarded as quinone-oximse.] The properties of pipitzahoic acid are such that it appears to belong to the group of benzoquinones; it was, therefore, somewhat surprising that Mylius obtained a well-characterised compound by the action of hydroxylamine on pipitzahoic acid, analysis of which gave results agreeing with the formula $C_{15}H_{21}O_3N$, and which Mylius considered as the "perezonoxime" (oxime of pipitzahoic acid) formed according to the reaction—

$$(C_{15}H_{20}O)O_2 + NH_2{\cdot}OH = (C_{15}H_{20}O)ON(OH) + H_2O.$$

Mylius has his doubts as to the correctness of this supposition, on account of the fact that by the action of boiling hydrochloric acid on this "perezonoxime," ammonium chloride and hydroxypipitzahoic acid, which has already been mentioned, and which will be described at a later period, were formed. He says, in fact:—" The action of concentrated hydrochloric acid on 'perezonoxime' takes place, therefore, according to the equation—

$$C_{15}H_{21}NO_3 + HCl + H_2O = C_{15}H_{20}O_4 + NH_3,HCl.$$

" It is a similar change to that which the amides undergo when, in consequence of the exchange of the amido-group for the hydroxyl-group, they become acids. Now, the hydroxypipitzahoic acid is really a description of acid, and it is easily conceivable that the hydroxylamine-derivative in question is its amide, and must be represented by the formula $C_{15}H_{19}O_3{\cdot}NH_2$. In this case the equation expressing its formation would be the following—

$$C_{15}H_{20}O_3 + NH_2{\cdot}OH = C_{15}H_{19}O_3{\cdot}NH_2 + H_2O."$$

Mylius further says, "A more thorough study of this compound is requisite before a decision in favour of the one or the other view can be arrived at."

The discovery that amidopipitzahoic acid is formed by the action of ammonia on anilido-, and on ortho- or para-toluido-pipitzahoic acid permits of a decision as to the real nature of Mylius's "perezonoxime" being easily arrived at; in fact, we have found by a comparison of the "perezonoxime," prepared according to Mylius's directions, with amido-pipitzahoic acid that the two substances are identical. Both preparations melted at 151° (according to Mylius "perezonoxime" melts at 153—154°). They possess the same colour; they crystallise in the same forms from alcohol; they behave in the same manner with solvents, with alkalis, and with concentrated sulphuric acid; and on boiling their alcoholic solutions with dilute sulphuric acid they both give hydroxypipitzahoic acid. We have also analysed Mylius's "pere-

zonoxime," and, as was to be expected, have obtained results which agree with the formula of amidopipitzahoic acid—

(1.) 0·1780 substance gave 0·4457 CO_2, and 0·1391 H_2O.
(2.) 0·4742 „ 21·6 c.c. N at 18°, and 754 mm.

	Calculated for $C_{15}H_{21}NO_3$.	Found. I.	Found. II.	Found by Mylius.	
C......	68·44	68·28	—	68·25	—
H	7·98	8·68	—	8·11	—
N......	5·33	—	5·28	—	5·54

As there is no longer any doubt that pipitzahoic acid is a quinone, proof of the identity of "perezonoxime" with amidopipitzahoic acid having thus been given, it follows that hydroxylamine may act on the quinones in a manner hitherto unknown, and may cause the introduction of the amido-group in place of one of the benzene hydrogen-atoms. The formation of amidopipitzahoic acid from ammonia and anilido- or ortho- or para-toluidopipitzahoic acid also gives promise of a method for the preparation of amidoquinones which appears to be of general application, as indeed is shown by an experiment with hydroxythymoquinone described later in the paper.

2. *Action of Hydroxylamine Hydrochloride on Pipitzahoic Acid.*

Having obtained the above-mentioned results with hydroxylamine, it appeared to us necessary to investigate the action of hydroxylamine hydrochloride in the hope of obtaining the pure quinoneoxime, which, if pipitzahoic acid were really a paraquinone, ought to belong to the class of nitrosophenols. We have, however, not as yet been successful. Various experiments which were carried out at temperatures ranging between 80° and 100° gave nothing but tarry products, although the reaction appears to take place better in the cold. The pipitzahoic acid was dissolved in about 20 times its weight of 50 per cent. cold alcohol, and after adding the requisite quantity of hydroxylamine hydrochloride, as well as a few drops of hydrochloric acid, the solution was set aside. At the end of two days its colour had become much darker, and when at the end of eight days the solution was poured into an excess of water, a red precipitate was formed, which became partially crystalline on being well shaken up. 5 grams of pipitzahoic acid yielded 4·9 grams of this precipitate, which consisted of a red, crystalline substance and some tar. As this tar proved to be about as soluble as the crystalline substance in alcohol, ether, benzene, chloroform, glacial acetic acid, carbon bisulphide and light petroleum, we have not yet been able to prepare the latter in the pure state.

3. *Action of Phenylhydrazine on Pipitzahoic Acid.*

Phenylhydrazine like hydroxylamine acts energetically on the quinones (*Ber.*, **16**, 1563; **17**, 1809, 3026); indeed, phenylhydrazine is decomposed by paraquinones such as benzo- tolu- and thymo-quinone with liberation of nitrogen, whereas phenylhydrazine hydrochloride reacts less energetically, but no well-characterised derivatives have been obtained from these quinones. On the other hand, according to Zincke, β-naphthaquinone, phenanthraquinone and other similar quinone-derivatives react well. Especially interesting is the identity which Zincke has proved to exist between the α-naphthaquinone-hydrazid, obtained by the action of α-naphthaquinone on phenylhydrazine hydrochloride, and benzene-azo-α-naphthol.* As Zincke says that he has prepared a well-characterised compound from phenylhydrazine and hydroxythymoquinone, which pipitzahoic acid so much resembles, we have treated pipitzahoic acid both with phenylhydrazine and also with phenylhydrazine hydrochloride.

If alcoholic solutions of pipitzahoic acid and phenylhydrazine be mixed, the liquid becomes dark-coloured and gas is evolved. 1 gram of pipitzahoic acid and 0·5 gram of phenylhydrazine produced 50 c.c. of nitrogen at 20°. The volume of nitrogen evolved is slightly greater than that which would represent the half of the total nitrogen in 0·5 gram of phenylhydrazine, on evaporation, the alcoholic solution gave nothing but a tarry product. Phenylhydrazine hydrochloride gave no better result; we added 1 gram of phenylhydrazine hydrochloride in 10 c.c. of water to 1 gram of pipitzahoic acid in 100 c.c. of alcohol, and after allowing the mixture to stand for two days at the ordinary temperature, we poured the dark-coloured solution into a large excess of water, whereby a brownish-red, tarry precipitate was

* I should like to take this opportunity of drawing attention to the following facts. The paraquinones are well known to be powerful oxidising agents. In the formation of α-naphtholazobenzene from α-naphthaquinone and phenylhydrazine, an intermolecular oxidation apparently takes place, the hydrazine-group losing one hydrogen-atom and the "quinone" oxygen-atom being reduced. It appears to me that the conditions under which the formation of nitrosophenols from the paraquinones and hydroxylamine takes place are exactly similar. Another fact must also here be taken into consideration, viz., that hydroxylamine is a reducing agent. I think agreement with other analogous reactions is better preserved in assuming that in the formation of the nitrosophenols from the quinones and hydroxylamine, through an intermolecular reducing process the "quinone" oxygen-atom changes to hydroxyl, than that in the formation of nitrosophenol from nitroso-dimethylaniline the "nitroso"-group changes to the "oxime"-group. It is still more difficult to explain the latter reaction, using the "oxime" formulæ for the paranitrosophenols, than the transformation of the nitrosophenols into the nitrophenols. The orthoquinones stand in close relationship to the diketones, and what may be proved for them does not necessarily apply to the paraquinones.—ANSCHÜTZ.

thrown down which appeared to be partially crystalline, but possessed no characteristics which invited an experimental investigation. In this experiment nitrogen was not evolved. Both with phenylhydrazine and its hydrochloride, pipitzahoic acid appears to behave in an exactly similar manner to benzo- tolu- and thymo-quinones.

Appendix.

Action of Ammonia on Anilidohydroxythymoquinone.

The exclusive formation of monamido-compounds by the action of aniline, ortho- and para-toluidine on pipitzahoic acid suggested the hypothesis that there might only be one benzene hydrogen-atom in pipitzahoic acid. As it appeared to us advantageous to compare the behaviour and properties of a known hydroxyquinone, in which also there was only one benzene hydrogen-atom, with that of pipitzahoic acid, we chose hydroxythymoquinone, as it has been the best investigated of the well-known similar quinones, and also can be obtained with comparative ease. Like pipitzahoic acid, hydroxythymoquinone forms with aniline and paratoluidine only a monanilido- or paratoluido-derivative. By boiling with dilute sulphuric acid the anilidohydroxythymoquinone is changed to dihydroxythymoquinone. So far we have only examined the action of alcoholic ammonia on anilidohydroxythymoquinone in order to thus generalise the reaction by which amidopipitzahoic acid is formed from anilidopipitzahoic acid.

Following the directions of H. Schulz we prepared from thymoquinone (*Ber.*, **16**, 898) first dimethylamidothymoquinone, and from this monhydroxythymoquinone, the melting point of which we found to be 164—165° (Schulz, 166°). Hydroxythymoquinone crystallises in yellow plates which closely resemble pipitzahoic acid. The requisite quantity of aniline was added to an alcoholic solution of monhydroxythymoquinone, and by this means we obtained the anilidohydroxythymoquinone described by H. Schulz. This compound crystallises in violet-black needles, which melt at 134—135°, and may easily be purified by recrystallisation from alcohol.

Diamidothymoquinone, $C_6\left\{\begin{matrix}CH_3\\C_3H_7\\O_2\\(NH_2)_2\end{matrix}\right.$, or *Amidohydroxythymoquinoneimide*, $C_6\left\{\begin{matrix}CH_3\\C_3H_7\\\left.\begin{matrix}O\\NH\end{matrix}\right\}\\OH\\NH\end{matrix}\right.$.—1 gram of anilidohydroxythymoquinone was

sealed up in a tube with 20 c.c. of the strongest alcoholic ammonia and heated in the water-bath; the tubes being now and then well shaken. After three hours' heating it was noticed that the colour of the solution had changed from red-brown to deep blue. At the end of two days a large quantity of dark-blue, shining crystals separated. In order to estimate the amount of separated aniline, we operated exactly as before in the case of amidopipitzahoic acid and in three experiments obtained the following results:—

(1.) 1 gram of the anilide with 15 c.c. of alcoholic ammonia gave 0·45 gram of the crystalline product and 0·95 gram of aniline hydrochloride, m. p. 193°.

(2.) 4 grams of the anilide in 60 c.c. of alcoholic ammonia gave 2·1 grams of the crystalline product and 0·95 gram of aniline hydrochloride.

(3.) 4 grams of the anilide in 40 c.c. of alcoholic ammonia gave 2·0 grams of the crystalline product and 1 gram of aniline hydrochloride.

We shall refer to these figures again.

The dark-blue crystals show a marked metallic lustre and give a green powder on pulverisation. They do not melt but sublime at a high temperature. In water, ether, benzene, chloroform, carbon bisulphide and light petroleum this compound is insoluble, and in hot alcohol it dissolves only to a very limited extent to a blue solution. Boiling glacial acetic acid on the other hand dissolves it in considerable quantities, and on cooling the solution nearly the whole crystallises out again in the form of black, shining plates. It dissolves very easily even in dilute hydrochloric acid, which is indicative of the presence of an amido-compound. Analysis of the crude product gave figures which agree with the formula of the hitherto unknown diamidothymoquinone.

(1.) 0·2031 gave 0·4563 gram CO_2 and 0·1398 H_2O.
(2.) 0·4384 „ 54·5 c.c. nitrogen at 7° and 743 mm.

	Calculated for $C_{10}H_{14}N_2O_2$.	Found. I.	Found. II.
C.........	61·85	61·27	—
H	7·21	7·64	—
N	14·43	—	14·86

Singularly enough, we obtained different results on analysing the substance crystallised from hot acetic acid and freed from the solvent by being placed in a vacuum of 10 mm. over soda-lime; these results agree, however, closely with one another.

(1.) 0·2149 gave 0·4630 CO_2 and 0·1450 H_2O.
(2.) 0·1857 „ 0·4000 „ 0·1193 „

The substance was now again recrystallised from acetic acid.

(3.) 0·1788 gave 0·3876 CO_2 and 0·1166 H_2O.
(4.) 0·2196 „ 23 c.c. N at 9·5° and 753 mm.

	Calculated for $C_{10}H_{14}N_2O_2$.	Calculated for $C_{10}H_{14}N_2O_2 + \frac{1}{2}(C_2H_4O_2)$.	Found. I.	II.	III.	IV.
C....	61·85	58·92	58·76	58·83	59·12	—
H ...	7·21	7·14	7·49	7·14	5·24	—
N ...	14·43	12·50	—	—	—	12·58

Of the substance used in analyses 3 and 4 a portion, after standing another two days over soda-lime in a vacuum, was pulverised in an agate mortar (when the smell of acetic acid was distinctly perceptible), and heated in a Liebig's drying tube at 100° (*Liebig's Annalen*, **228**, 303) under a pressure of 30 mm. in a slow current of air until the weight became constant—

(1.) 0·5756 lost 0·0768 of its weight.
(2.) 0·3676 „ 0·0492.

	Calculated for $C_{10}H_{14}N_2O_2 + \frac{1}{2}(C_2H_4O_2)$.	Found. I.	II.
$C_2H_4O_2$	13·39	13·34	13·44

The substance thus freed from acetic acid was again analysed :—

(1.) 0·1956 gave 0·4412 CO_2 and 0·1269 H_2O.
(2.) 0·2457 „ 29·3 c.c. N at 2° and 766 mm.

	Calculated for $C_{10}H_{14}N_2O_2$.	Found. I.	II.
C	61·85	61·51	—
H	7·21	7·21	—
N	14·43	—	14·97

These figures afford proof that the substance is either diamidothymoquinone or the isomeric amidohydroxythymoquinone-imide :—

$$C\begin{cases} CH_3 \\ C_3H_2 \\ O_2 \\ (NH_2)_2 \end{cases} \quad \text{or} \quad C_6\begin{cases} CH_3 \\ C_3H_7 \\ \left.\begin{matrix} O \\ NH \end{matrix}\right\} \\ OH \\ NH_2 \end{cases},$$

and that it crystallises from acetic acid with $\frac{1}{2}$ mol. of the solvent.

Ammonia acted therefore in a somewhat different manner on anilidohydroxythymoquinone to what it did on anilidopipitzahoic acid; the aniline-group was in this case displaced by the amido-group, and thus far the action of ammonia on these aniline-derivatives was the same. Whilst, however, in the case of anilidopipitzahoic acid, the action of the ammonia was restricted to the production of amidopipitzahoic acid, the anilidohydroxythymoquinone was still further altered. Now whether the second nitrogen-atom displaced the quinone oxygen-atom in the form of the imido-group or the hydroxy-group in the form of the amido-group, we must leave for the present undecided. The properties of the product, however, are more those of a diamido-compound, and we shall therefore speak of it as diamidothymoquinone.

The yield of diamidothymoquinone is by no means quantitative, a dark brown, amorphous substance, easily soluble in alcohol, being also produced, and this we did not examine further. The following tabulation of the amounts of diamidothymoquinone and of aniline hydrochloride obtained from the above-mentioned operations show that, although the results of experiments No. 2 and 3 are materially better than that of No. 1, the yield only amounts to five-sevenths of that theoretically possible.

	Calculated for $C_{10}H_{11}O_3 \cdot NH \cdot C_6H_5$.	Found. I.	II.	III.
$C_{10}H_{14}N_2O_3$	71·5	45·0	52·0	50·0
$C_6H_5NH_2 \cdot HCl$....	47·7	15·0	23·8	25·0

Diamidothymoquinone is a feeble base, and dissolves in hydrochloric acid with a red colour, but by evaporating the solution on the water-bath the salt is decomposed. On boiling it with concentrated caustic potash it is dissolved, ammonia being given off, and on acidulating with hydrochloric acid a red precipitate is thrown down. Stannous chloride in hydrochloric acid reduces it at once; it being dissolved to a colourless solution. Agitation of this solution with ether, and subsequent evaporation of the ether showed that nothing had been extracted, but if the tin is precipitated with sulphuretted hydrogen and the sulphides of tin filtered off, the clear colourless solution is very rapidly oxidised on exposure to the atmosphere and the solution again turns red, the hydroquinone being oxidised to quinone.

Hydroxypipitzahoic Acid.

In his investigation of the compounds of the quinones with amines Zincke found that on boiling the alcoholic solutions of these derivatives with dilute sulphuric or hydrochloric acid, the amido-groups are displaced by hydroxyl.

$$C_6H_3\begin{cases}O_2\\NR'R''\end{cases} + H_2O = C_6H_3\begin{cases}O_2\\OH\end{cases} + NR'R''H.$$

In this equation R′ and R″ may represent either hydrogen-atoms or monad hydrocarbon-groups.

If an alcoholic solution of anilidopipitzahoic acid be boiled with a little dilute sulphuric acid, the colour of the solution changes very rapidly to orange. On addition of water, an apparently homogeneous red precipitate is formed which may be easily extracted with ether, and crystallises very beautifully from this solvent. This reaction takes place just as easily with the two toluides of pipitzahoic acid, and also, though somewhat more slowly, in the case of amidopipitzahoic acid. The substance thus produced was recrystallised from alcohol, and was obtained in red crystals melting at 127—129°. Analysis gave the following results:—

(1.) 0·1920 gave 0·4726 CO_2 and 0·1414 H_2O.
(2.) 0·1852 gave 0·4558 CO_2 and 0·1350 H_2O.

	Calculated for $C_{15}H_{20}O_4$.	Found. I.	Found. II.
C	68·18	67·13	67·12
H	7·57	8·18	8·10

The results of both analyses are accordant, but do not agree with the formula of hydroxypipitzahoic acid, $C_{15}H_{20}O_4$. In preparing this substance a second time we used benzene as the solvent, and in dissolving the crude product we found that the hydroxypipitzahoic acid was mixed with a pale yellow substance, very insoluble in benzene, which being very easily soluble in alcohol we had not previously observed. The substance after having been purified by repeated recrystallisation from benzene, melted at 124°, but the results of the analysis were still less in accordance with the formula $C_{15}H_{20}O_4$.

(1.) 0·2261 gave 0·5512 CO_2 and 0·1656 H_2O.
(2.) 0·2319 when burned with $PbCrO_4$ gave 0·5600 CO_2 and 0·1709 H_2O.

The substance used for analysis 3 was now again crystallised from benzene.

(3.) 0·1515 gave 0·3687 CO_2 and 0·1119 H_2O.

	Calculated for $C_{15}H_{20}O_4$.	Found. I.	Found. II.	Found. III.
C	68·18	66·47	66·00	66·37
H	7·57	8·13	8·18	8·20

We now altered our method of preparing the acid in so far that we used the least possible quantity of sulphuric acid. The anilidopipitzahoic acid was dissolved in dilute alcohol, and while the solution was boiling in a retort connected with an inverted condenser, dilute sulphuric acid was slowly added drop by drop until the blue colour of the solution changed to red. The product of the reaction separated almost completely as the solution cooled, and after drying and recrystallising from benzene melted at 138°, but in other respects it had the same appearance as the two other specimens melting at 124° and 129° respectively. By this method of preparation we did not obtain the least particle of the yellow substance above referred to; it is also noteworthy that we required far less sulphuric acid when working in this manner than in preparing the two former specimens. The analysis of the specimen melting at 138° gave the following results:—

(1.) 0·1579 gave 0·3922 CO_2 and 0·1121 H_2O.

The substance was now recrystallised from benzene.

(2.) 0·1447 gave 0·3588 CO_2 and 0·1010 H_2O.

	Calculated for $C_{15}H_{20}O_4$.	Found. I.	Found. II.
C	68·18	67·74	67·63
H	7·57	7·88	7·75

According to these figures the product must have been almost pure hydroxypipitzahoic acid, the melting point of which, according to Mylius, is 133—134°. In one experiment with 3·3 grams of anilidopipitzahoic acid we obtained 0·9 gram aniline hydrochloride, instead of 1·26 gram. The reaction may be represented by the following equation:—

$$C_{15}H_{19}O_3\cdot NH\cdot C_6H_5 + H_2O + HCl = C_{15}H_{20}O_4 + C_6H_5NH_3Cl.$$

In another experiment we used dilute acetic acid as the solvent for the anilidopipitzahoic acid instead of dilute alcohol, 3 grams being dissolved in 40 c.c. of acetic acid and 40 c.c. of water; 10 c.c. of sulphuric acid, composed of 5 c.c. of concentrated sulphuric acid and 5 c.c. of water, was required in order to complete the reaction. But dilute alcohol is preferable, for the product after crystallisation from benzene melted at 129—130°, and a comparatively large quantity of the above-mentioned yellow substance was formed. The decomposition was complete, however, for we obtained 1·1 gram aniline hydrochloride instead of 1·11 gram.

There was not enough of the yellow substance formed in the preparation of hydroxypipitzahoic acid for a careful examination of its properties. It is certainly not the yellow substance melting at 143°,

mentioned by Mylius, which was prepared by heating hydroxypipitzahoic acid with concentrated sulphuric acid, and named by him "perezinone." The yellow substance observed by us does not melt, and is only decomposed on a high temperature being reached; it is easily soluble in alcohol and acetic acid, but is almost insoluble in ether and especially in benzene.

Hydroxypipitzahoic acid dissolves readily in ether, chloroform, glacial acetic acid, benzene and warm alcohol, and is sparingly soluble in carbon bisulphide and light petroleum. It crystallises best from benzene. In solutions of the alkalis the hydroxypipitzahoic acid forms salts, the aqueous or alcoholic solutions of which are of a purple colour. With solution of barium hydroxide, it forms a green precipitate which is easily soluble in alcohol. We were not able to obtain a well-characterised product by heating it with excess of acetic acid anhydride in a sealed tube at 100°. Hydroxypipitzahoic acid does not react with aniline; its alcoholic solutions are decolorised by reducing agents, but we were unsuccessful in all our attempts to isolate the product of reduction.

Action of Bromine on Pipitzahoic Acid and Hydroxypipitzahoic Acid.

The opinions on the constitution of pipitzahoic acid, founded on Weld's experiments, which we expressed in the commencement of this paper, led us to accept the fact that whether we assume that one, two, or three of the benzene hydrogen-atoms in pipitzahoic acid are displaced by hydrocarbon-groups, one of these must contain a doubly-linked pair of carbon-atoms. In order to test experimentally the truth of this hypothesis, we very gradually mixed molecular quantities of pipitzahoic acid and bromine, both dissolved in chloroform and cooled with a mixture of ice and salt, and observed that hydrogen bromide was not evolved on the chloroform being allowed to evaporate, even after 24 hours' standing.

Dibromide of Pipitzahoic Acid.—The chloroform solution of pipitzahoic acid becomes dark coloured after treatment with bromine, and the residue after evaporation of the chloroform is also dark brown-coloured.

(1.) 1 gram of pipitzahoic acid treated with 0·65 gram of bromine gave 1·6 grams of the dry product.

(2.) 5 grams of pipitzahoic acid treated with 3·20 grams of bromine gave 8·20 grams of the dry product.

On estimating the bromine in this dry product by Carius's method the following result was obtained:—

0·2059 gave 0·2042 AgBr, equal to 0·0871 Br.

	Calculated for $C_{15}H_{20}O_3Br_2$.	Found.
Br	39·21	42·30

The brown-coloured, crude additive product was now triturated with cold alcohol, whereby we obtained a canary-yellow powder which when dry melted between 107° and 109°.

0·2183 gave 0·1918 AgBr, equal to 0·0817 Br.

	Calculated for $C_{15}H_{20}O_3Br_2$.	Found.
Br	39·21	37·42

Experiments made with a view of purifying by recrystallisation this additive product, which is readily soluble in almost all solvents, showed the ease with which it is decomposed with separation of hydrogen bromide.

Dibromide of Hydroxypipitzahoic Acid.—This additive product was prepared in the same way as the dibromide of pipitzahoic acid, and it is just as unstable as the latter. On evaporation of its chloroform solution at the ordinary temperature, it remains as a red, amorphous powder.

1 gram of hydroxypipitzahoic acid and 0·6 gram of bromine gave 1·5 grams of the dry additive product.

5·05 grams of hydroxypipitzahoic acid and 3 grams of bromine gave 8 grams of the dry additive product.

These figures prove that the bromine is readily taken up. An estimation of the bromine in the dry crude product gave the following result:—

0·2160 gram substance gave 0·1941 gram AgBr, equal to 0·0826 gram Br.

	Calculated for $C_{15}H_{20}O_4{\cdot}Br_2$.	Found.
Br	37·73	38·29

The dibromide of hydroxypipitzahoic acid behaves with solvents very similarly to the dibromide of pipitzahoic acid. It is easily soluble in alcohol, ether, chloroform and glacial acetic acid, but less easily in light petroleum and carbon bisulphide; we could not, however, recrystallise it from any of these solvents. It melted with decomposition between 140° and 146°. We endeavoured to obtain it pure by fractional crystallisation, and the following analytical results are of fractions obtained from carbon bisulphide (Nos. 1 and 2) and dilute alcohol (Nos. 3, 4, 5 and 6).

(1.) 0·2048	gave	0·1570 AgBr,	equal to	0·0670 Br.
(2.) 0·1981	„	0·1536 „	„	0·0655 „
(3.) 0·1726	„	0·1271 „	„	0·0542 „
(4.) 0·1507	„	0·1018 „	„	0·0434 „
(5.) 0·1994	„	0·1280 „	„	0·0545 „
(6.) 0·0977	„	0·0526 „	„	0·0226 „

	Calculated for $C_{15}H_{20}O_4 \cdot Br_2$.	Found. I.	II.	III.	IV.	V.	VI.
Br......	37·73	32·71	33·06	31·40	28·80	27·32	23·13

The instability of the bromide is clearly proved by these figures: each successive fraction from alcohol contains less bromine, the melting point sinking at the same time (the substance used for analyses 1, 2, 3, 4 melted between 140° and 144°, the substance No. 5 melted at 135°, and that following (No. 6) at 127°).

Summary.

The acid properties of pipitzahoic acid were recognised by the discoverer of this substance, Rio de la Loza. The formula deduced by Weld from his analyses of the acid, and also from the analyses of several of its salts, is confirmed by our researches. It may be inferred from Weld's experiments that pipitzahoic acid is a monobasic acid, although at the same time it is evident that it does not belong to the group of carboxylic acids but to that of the phenols, as its alkali metal salts are decomposed by carbonic anhydride. The beautiful golden-yellow colour, in addition to the fact that pipitzahoic acid contains only carbon, hydrogen, and oxygen, suggested that it might be a quinone; this we have proved to be the case by our experiments. Hence the functions of the three oxygen-atoms are established.

Discussing the constitution of pipitzahoic acid on the basis of the above-mentioned facts, it appeared probable that it belonged to the group of hydroxybenzoquinones, and that it might contain one, two or three side-chains. The action of amines was therefore studied in the hope of obtaining evidence of the number of benzene hydrogen-atoms still present. Our experiments show that pipitzahoic acid reacts with aniline, and ortho- and para-toluidine with extreme readiness, exactly as the better-known quinones do, and that always *only* a single hydrogen-atom becomes displaced. It may with justice be maintained that a hydroxybenzoquinone which with aniline, even when this is present in large excess, gives only a *mon*-anilide, contains also only *one* benzene hydrogen-atom. It may be further suggested that the dihydroxyquinone, obtained by the action of acids on this monanilido-oxybenzo-

quinone, cannot have another hydrogen-atom displaceable by the anilido-group: hydroxypipitzahoic acid does not, in fact, react with aniline. Hence it follows that most probably there are two hydrocarbon side-chains present in pipitzahoic acid. As to the nature of these side-chains, it has been pointed out that, however many may be present in pipitzahoic acid, there must be at all events one side-chain which contains a doubly-linked pair of carbon-atoms: proof of the truth of this conclusion is given by the behaviour of pipitzahoic acid and hydroxypipitzahoic acid with bromine. Pipitzahoic acid contains therefore most probably two side-chains of which the one is a hydrocarbon radicle of the formula C_nH_{2n+1}, the other a hydrocarbon radicle of the formula C_nH_{2n-1}. We are unable at present to express any opinion as to the nature and position of these radicles.

In order to prove the truth of our ideas of the nature of pipitzahoic acid by a comparison of its properties with those of a hydroxybenzoquinone of known constitution containing two hydrocarbon side-chains, we have included the best investigated hydroxybenzoquinone, hydroxythymoquinone, in our experiments. Crystallised from dilute alcohol, pipitzahoic acid is in colour and crystalline form so like hydroxythymoquinone crystallised from the same solvent, that the two are very difficult to distinguish with the unaided eye. Again dihydroxythymoquinone, like hydroxypipitzahoic acid, is a red substance. With reducing agents pipitzahoic acid and hydroxythymoquinone behave very similarly, both being converted into colourless hydroquinones, easily soluble in water, and which on account of their instability have not yet been isolated. We have not yet succeeded in preparing ethers of hydroxythymoquinone. On the other hand, we have obtained from pipitzahoic acid by the action of acetic anhydride, a colourless compound in good measurable crystals, which according to the analysis might be an acetic ether. Further we have succeeded in obtaining by the action of ethyl bromide on the silver salt, a colourless well-crystallised substance, unfortunately in too small quantity for an analysis. We are, however, inclined to doubt whether these derivatives really are ethers of pipitzahoic acid: firstly, because we have not succeeded in regenerating pipitzahoic acid from them; and secondly, because they are colourless, whereas they ought to be yellow or orange if the quinone oxygen-atoms are still present. Hydroxythymoquinone and pipitzahoic acid form with aniline and paratoluidine only a mon-anilide or monoparatoluide. Hydroxythymoquinone is prepared in the same way from anilidohydroxythymoquinone as hydroxypipitzahoic acid from the anilide of pipitzahoic acid: treated with alcoholic ammonia, the aniline-group is displaced in the anilides of both these hydroxyquinones by the amido-group; but in the case of the anilidohydroxythymoquinone the reaction goes

further, one of the oxygen-atoms, probably that of the hydroxyl-group, being displaced by amidogen.

All these facts tend to show that a great analogy exists in the behaviour of pipitzahoic acid and of hydroxythymoquinone, and suggest accordingly that the constitution of these substances is analogous.

LXVIII.—*On the Analysis of Alloys and Minerals containing the Heavy Metals, Selenium, Tellurium, &c.*

By Thomas Bayley.

The metals and metalloids (semi-metals) which can be precipitated as sulphides from aqueous liquids are naturally divided into two groups. On the one hand there are those elements forming sulphides insoluble in alkaline sulphides, and on the other the elements whose sulphides are soluble.

Methods have been devised for separating the one group from the other by taking advantage of these differences; such methods have not been extensively employed in quantitative analysis, although they have proved useful in the qualitative testing of mixtures. This partial failure is due to the difficulty of removing the sulphides of the soluble groups when once they have been precipitated in admixture with the other sulphides. Repeated digestions with the alkaline sulphide are necessary if anything approaching to a complete separation is desired.

It is possible, however, by a modification of this method which I have used for some time, to obtain good results in the analysis of samples of bronze, gun-metal, fusible and other alloys. Instead of precipitating both classes of sulphides together and subsequently treating with the solvents, it is better to altogether prevent the precipitation of the elements forming sulpho-salts. Experience has shown that the process conducted on this principle is at once accurate and very easy of execution. The method may be called the sulphide of sodium method, because in general this is the most convenient solvent to employ.

About 2·5 grams of the sample is dissolved in the smallest practicable quantity of nitric acid of 1·2 sp. gr., or aqua regia may be used when more convenient, as for instance when tin is present, or when an estimation of the silica in a mineral is desired.

Ores containing galena are best dissolved by hydrochloric acid and

potassium chlorate at a boiling temperature, the solution being sufficiently dilute to dissolve the salt of lead as fast as it is formed. In this way a protective coating is avoided and the operation accelerated. To the clear and sufficiently dilute solution of the metals, after filtration from silica, silver chloride, barium sulphate and insoluble matters generally, 5 grams of tartaric acid and 5 grams of citric acid are added and then sufficient caustic soda to approximately neutralise the liquid, which at this stage should be diluted to not less than 500 c.c. An ounce of solid caustic soda is next dissolved in the neutralised solution, which is heated to boiling, and sulphuretted hydrogen conducted through it until precipitation has taken place and the supernatant liquid has been transformed into a yellow solution of alkaline sulphydrate. The object of thus adding the soda in two operations is to ensure the presence of a known excess of alkali during the precipitation by sulphuretted hydrogen. The boiling should be continued (in a porcelain basin) for at least half-an-hour, and until the sulphides assume a heavy, granular condition and sink rapidly to the bottom, when the ebullition is discontinued.

If water has been added from time to time to replace that lost by evaporation, rapid collection and washing of the precipitate are practicable without rupture of good Rhenish filter-paper.

The precipitate contains the copper, lead, zinc, and iron sulphides, and also the whole of the gold and platinum contained in the sample; nickel, if present, demands the previous separation by sulphuretted hydrogen of the metals forming sulphides insoluble in dilute acids. The solution contains the arsenic, antimony, tin, selenium, tellurium, &c.

(*a.*) *Treatment of the Precipitate.*—After two or three washings, the sulphides of lead, copper, &c., are removed from the paper into a wide beaker by a jet of water, the filter is burnt, the ash added to the beaker, and the mixture is covered up and allowed to digest after addition of nitric acid. Copper and lead salts are formed on warming, and when the sulphur has become yellow, a sufficient excess of dilute sulphuric acid is added. The beaker being now uncovered, evaporation takes place, the nitric acid is expelled, and the sulphuric acid concentrated. Enough water is now cautiously employed to produce a dilute acid of about 1 part of acid to 8 parts of water, and in order to ensure the complete separation of lead, the acid is once more concentrated and diluted to the same extent. The lead sulphate, mixed with all the gold and platinum, is next filtered off. These precious metals may be separated from the lead by solution of the latter in acetate of ammonium, or by treatment of the mixed precipitate with a very little aqua regia, which, however, causes a few milligrams of lead to dissolve. The gold is separated by ferrous sulphate or oxalic acid, and the platinum then determined by well-known methods. I

prefer treatment with ammonium acetate as the lead sulphate is thereby purified.

(*b.*) *Treatment of the Filtrate.*—This is acidified with dilute sulphuric acid, and the sulphides, after digestion at a gentle heat to promote clotting, are separated by filtration and washed. They may be treated by any suitable method; the following is one I have applied:—

The sulphides are oxidised by concentrated nitric acid and bromine, together with the filter-paper if the precipitate cannot be removed without loss. Subsequent addition of tartaric acid is essential in presence of antimony. The solution is treated with ammonia, filtered, and the arsenic precipitated with magnesia mixture, the precipitate being dissolved in hydrochloric acid and reprecipitated after filtration; this second filtrate is mixed with the first as it may contain a milligram or two of selenium or tellurium, but not more. The mixed filtrates from the arsenic is concentrated and freed from ammonia by evaporation, and an ounce of oxalic acid is dissolved in it. It is then saturated with sulphuretted hydrogen whilst boiling, which precipitates antimony, selenium, and tellurium, leaving tin in solution. The tin is recovered by sulphuretted hydrogen, after evaporation with strong sulphuric acid to destroy the oxalic acid, and weighed as SnO_2 after ignition.

The selenium and tellurium are separated from antimony by solution in aqua regia, evaporation with hydrochloric acid in presence of potassium or sodium chloride, and precipitation with sulphurous acid. They are afterwards separated from each other by boiling with potassium cyanide, precipitation of the selenium by hydrochloric acid, and reprecipitation of the tellurium by sulphurous anhydride. The antimony is precipitated by sulphuretted hydrogen, and weighed as sulphide or as tetroxide.

The following test analyses were made by this method:—

	Taken.	Found.	Taken.	Found.
Sn....	0·5000 gram	0·5001 gram	0·2500 gram	0·2507 gram.
Pb....	0·5000 ,,	0·4998 ,,	0·5000 ,,	0·5002 ,,
Au ...	0·1000 ,,	0·0998 ,,	0·0100 ,,	0·0097 ,,

	Taken.	Found.	
Sn......	0·5000 gram	0·4998 gram.	
Pb	0·5000 ,,	0·4975 ,,	
Pt......	0·2000 ,,	0·1985 ,,	precipitated as sulphide [and ignited.
Au	0·2000 ,,	0·1996 ,,	

By Mr. J. C. Welch—

	Taken.	Found.	
Pt....	0·1145 gram	0·2145 gram (not separated.)	
Au...	0·1000 ,,		
Sn....	0·2500 ,,	0·2492 ,,	
As_2O_3.	0·2500 ,,	0·2484 ,,	
Pb ...	0·5135 ,,	0·4887 ,,	(accidental loss).
Cu ...	0·5200 ,,	0·5199 ,,	
Se....	0·0800 ,,	0·0750 ,,	
Te ...	0·2000 ,,	0·2032 ,,	
Sb....	0·2500 ,,	0·2527 ,,	weighed as Sb_2S_3.

In analyses like the latter, the precipitates insoluble in sodium sulphide should be redissolved and reprecipitated to ensure complete separation of selenium and tellurium.

German Silver.—Although usually almost perfectly free from more than traces of Sn, Sb, or As, this alloy may be taken as the type of a substance containing nickel. The solution of 1 gram or so of the German silver in the smallest possible quantity of nitric acid is mixed with a few drops of ammonia and one or two drops of sulphuric acid (the ammonium sulphate promotes the passage of the current), and the copper then precipitated by electrolysis with two large Daniell cells, any undeposited traces being precipitated by sulphuretted hydrogen, and estimated colorimetrically. If sulphuretted hydrogen has been used it is removed by a little bromine-water, and ammonia is added in slight excess, and then 10 or 12 oz. of redistilled acetic acid (B.P. 33 per cent.). The volume before adding the acetic acid should be about 50 c.c. The zinc is completely precipitated by sulphuretted hydrogen *in the cold.* A pure white zinc sulphide is thus obtained, and since no fixed matter has been introduced, evaporation to dryness with sulphuric acid, ignition and weighing of the nickel as sulphate, gives uniformly satisfactory results. Any iron present must be separated either before or after the evaporation.

Certain commercial alloys are said to contain aluminium, chemical analysis is usually not capable of detecting this metal, although *it is said* to confer extraordinary properties on the alloy. I cannot speak as to recent samples of American origin.

I have pleasure in acknowledging the careful and skilful assistance I have received from my assistant, Mr. J. C. Welch, in many analyses by these methods.

LXIX.—*Further Contributions to the Knowledge of Cyanuric Chloride and other Cyanuric Derivatives.*

By Harold H. Fries.

In a recent communication (Trans., 1886, 314) on the action of cyanuric chloride on α-naphthylamine, I described a series of mono-, di-, and tri-naphthylamidocyanuric derivatives. I have now succeeded in obtaining a similar series from β-naphthylamine, toluylenediamine, and phenylhydrazine.

Before describing these compounds, I would call attention to a modification of the method of preparing cyanuric chloride which I have adopted. Gautier (*Annalen*, **141**, 122) suggested that cyanuric chloride should be made by passing dry chlorine into a solution of hydrogen cyanide in ether. The vessel containing the ether is surrounded by ice, dry hydrogen cyanide is passed in until the liquid is saturated, and then chlorine. Throughout the greater part of this operation the hydrogen cyanide is in excess, and a large quantity of a double compound of cyanogen chloride and hydrogen cyanide is formed. Claësson (*Bihang till K. Svenska Vet. Akad. Handlinger*, **10**, No. 5) uses chloroform in place of ether. Chlorine is more soluble in chloroform than in ether, and an excess of this gas, avoided by Gautier, is found by Claësson to increase the yield of cyanuric chloride considerably. Now a still better result is obtained if the chlorine be in excess from the commencement. When this is done the cyanuric chloride produced is almost entirely free from bye-products.

I lead chlorine into the chloroform first, then hydrogen cyanide and chlorine together, always taking care to have the latter in excess. The process is continued as long as there remains any unchanged hydrogen cyanide, which point is marked by the stoppage of the evolution of hydrogen chloride. In many cases the cyanuric chloride separates from the chloroform during the experiment in beautiful crystals.

Action of Cyanuric Chloride on β-Naphthylamine.

From the analogy between the behaviour of β- and α-naphthylamine it was to be expected that derivatives of cyanuric chloride would be obtained with the former compound analogous to those already produced with the latter. Thus the following compounds were possible:—

$C_3N_3Cl_2\cdot NH\cdot C_{10}H_7$	$C_3N_3Cl(NH\cdot C_{10}H_7)_2$	$C_3N_3(NH\cdot C_{10}H_7)_3$
Primary β-naphthylamidocyanuric chloride.	Secondary β-naphthylamidocyanuric chloride.	β-Naphthylmelamine.

Primary β-Naphthylamidocyanuric Chloride.—Solutions of cyanuric chloride and β-naphthylamine in dry ether are quickly mixed together in the proportion of 1 molecule of the chloride to 2 molecules of β-naphthylamine. A precipitate of β-naphthylamine hydrochloride is formed which is removed by filtration and the filtrate evaporated to dryness. The residue crystallised several times from hot alcohol gives beautiful, colourless crystals, melting at 154°, of the primary β-naphthylamidocyanuric chloride, $C_3N_3Cl_2{\cdot}NH{\cdot}C_{10}H_7$.

	Theory.		Experiment.		
			I.	II.	III.
C_{13}......	156	53·61	53·51	—	—
H_8......	8	2·75	2·99	—	—
N_4......	56	19·24	—	19·61	—
Cl_2	71	24·40	—	—	24·48
	291	100·00			

Secondary β-Naphthylamidocyanuric Chloride.—In the preparation of this compound ethereal solutions are mixed slowly drop by drop, and in the proportion of 4 molecules of β-naphthylamine to 1 molecule of cyanuric chloride. The precipitated β-naphthylamine hydrochloride is removed as before, and the residue, after evaporation, recrystallised several times from alcohol. In this way colourless needles, melting at 178°, are formed of secondary β-naphthylamidocyanuric chloride, $C_3N_3Cl(NH{\cdot}C_{10}H_7)_2$.

	Theory.		Experiment.		
			I.	II.	III.
C_{23}......	276	69·43	69·11	—	—
H_{16}	16	4·02	4·41	—	—
N_5......	70	17·60	—	17·48	—
Cl......	35·5	8·95	—	—	9·18
	397·5	100·00			

β-Naphthylmelamine.—One molecular proportion of cyanuric chloride is thoroughly mixed with six molecular proportions of β-naphthylamine and heated in a closed tube at 150° for about three hours. The contents of the tube is then washed with hot water and dried. The crude melamine thus obtained is crystallised from nitrobenzene and washed with alcohol. Addition of alcohol to the nitrobenzene promotes the crystallisation of the melamine, which consists of beautiful needles melting at 209°. Its formula is $C_3N_3(NH{\cdot}C_{10}H_7)_3$.

	Theory.		Experiment.		
			I.	II.	III.
C_{33}......	396	78·57	78·36	—	—
H_{24}	24	4·76	5·27	—	—
N_6......	84	16·67	—	16·53	16·73
	504	100·00			

Action of Cyanuric Chloride on Toluylenediamine.

It seemed interesting to see if a similar series of compounds could be obtained with toluylenediamine.

Primary Toluylenediamidocyanuric Chloride.—Solutions of cyanuric chloride in absolute ether and of toluylenediamine in absolute alcohol are mixed together drop by drop in the proportion of 1 molecule of the chloride to 2 molecules of the diamine. The precipitate which forms is removed, and the filtrate, on evaporation, gives the primary toluylenediamidocyanuric chloride, $C_3N_3Cl_2\cdot NH\cdot C_7H_6\cdot NH_2$, which decomposes when heated without showing a defined melting point.

	Theory.		Experiment.		
			I.	II.	III.
C_{10}......	120	44·45	44·12	—	—
H_9......	9	3·33	3·84	—	—
N_5......	70	25·93	—	25·99	—
Cl_2	71	26·29	—	—	26·48
	270	100·00			

Secondary Toluylenediamidocyanuric Chloride. — Theoretical proportions of the solutions of cyanuric chloride and toluylenediamine are mixed and the precipitated hydrochloride removed as in the case of the preceding derivative. The crude compound is separated from the filtrate by evaporation, and is obtained in beautiful needles by recrystallisation from alcohol. These decompose when heated at about 172°. This derivative has the formula $C_3N_3Cl(NH\cdot C_7H_6\cdot NH_2)_2$.

	Theory.		Experiment.		
			I.	II.	III.
C_{17}......	204	57·38	57·21	—	—
H_{18}	18	5·07	5·38	—	—
N_7......	98	27·56	—	27·83	—
Cl	35·5	9·99	—	—	10·23
	355·5	100·00			

Toluidylmelamine.—A mixture of toluylenediamine and cyanuric chloride is enclosed in a tube and heated at 100° for several hours. The product is washed with water, then treated with boiling alcohol and filtered, when the filtrate deposits toluidylmelamine in crystals on cooling. These are purified by several recrystallisations. They show no distinct melting point. Their formula is $C_3N_3(NH{\cdot}C_7H_6{\cdot}NH_2)_3$.

	Theory.		Experiment. I.	Experiment. II.
C_{24}	288	65·30	65·32	—
H_{27}	27	6·13	6·19	—
N_9	126	28·57	—	28·82
	441	100·00		

Action of Cyanuric Chloride on Phenylhydrazine.

I have also succeeded in producing a series of compounds analogous to those already described, in which a phenylhydrazine residue replaces the chlorine of cyanuric chloride.

Primary Phenylhydrazine Cyanuric Chloride.—Ethereal solutions of phenylhydrazine and cyanuric chloride are mixed together drop by drop, and the precipitate of phenylhydrazine hydrochloride removed by filtration. On evaporation, the filtrate yields a crystalline precipitate which is purified by washing with water, alcohol and ether. It gives no defined melting point, and has the formula

$$C_3N_3Cl_2{\cdot}NH{\cdot}NH{\cdot}C_6H_5.$$

	Theory.		Experiment. I.	Experiment. II.	Experiment. III.	Experiment. IV.
C_9....	108	42·19	41·92	—	—	—
H_7...	7	2·74	3·01	—	—	—
N_5...	70	27·34	—	27·28	27·03	—
Cl_2...	71	27·73	—	—	—	28·02
	256	100·00				

Secondary Phenylhydrazine Cyanuric Chloride.—Theoretical proportions of the two substances in ethereal solution are rapidly mixed together, and, after removal of the hydrochloride formed, the filtrate evaporated to dryness. The residue recrystallised from alcohol gives needles of secondary phenylhydrazine cyanuric chloride.

$$C_3N_3Cl(NH{\cdot}NH{\cdot}C_6H_5)_2.$$

	Theory.		Experiment. I.	II.	III.	IV.
C_{15}....	180	54·96	54·62	—	—	—
H_{14}....	14	4·27	4·44	—	—	—
N_7....	98	29·97	—	29·86	30·23	—
Cl....	35·5	10·84	—	—	—	11·12
	327·5	100·00				

Anilylmelamine.—When the primary derivative is heated in a closed tube with phenylhydrazine at 100° anilylmelamine is formed, and is purified by successive crystallisations from alcohol. It has the formula $C_3N_3(NH{\cdot}NH{\cdot}C_6H_5)_3$.

	Theory.		Experiment. I.	II.
C_{21}........	252	63·15	63·08	—
H_6........	6	5·26	5·64	—
N_9........	126	31·59	—	31·91
	384	100·00		

Chemical Laboratory,
University of Berlin,
July, 1886.

LXX.—*Further Observations on the Action of Hexabromacetone on Urea.*

By Alfred Senier.

In a recent communication (*ante*, p. 693) I described a series of experiments showing that of the two isomeric cyanuric acids which Herzig (*Ber.*, **12**, 170) claims to have obtained by the action of hexabromacetone on urea, the one—the α-acid—is identical with ordinary cyanuric acid, whilst in the case of the other—the β-acid—further experiments were needed before a decisive opinion could be formed. These have now been made. I have prepared several specimens of the β-acid, carefully attending to the directions given by Herzig; they were all similar in appearance, and consisted of crystals unlike cyanuric acid, and exhibited generally the properties which Herzig observed. On repeated recrystallisations from water, however, the crystals were found

gradually to assume the character of the ordinary acid and the other distinctions one by one to disappear. The properties given by Herzig as distinguishing the β from the α and from the ordinary acid are:—

I. When heated it does not yield cyanic acid.
II. When treated with phosphorus pentachloride cyanuric chloride is not formed.
III. It does not give Hofmann's test for cyanuric acid.
IV. The crystals do not contain water.
V. It is more soluble in alcohol than either the (α) or the ordinary acid.
VI. A barium salt of constant composition could not be obtained.

I. *Action of Heat.*

None of the specimens which I have examined appeared to yield cyanic acid when heated in small tubes until they had been three or four times recrystallised from water; when this was done, however, the odour of cyanic acid was easily obtained, and could be recognised beyond any doubt.

II. *Action of Phosphorus Pentachloride.*

By carefully treating the product obtained by heating the β-acid with phosphorus pentachloride in a closed tube, in accordance with the directions of Beilstein (*Annalen*, **116**, 357), I have isolated cyanuric chloride as announced in my previous paper. The contents of the tube are in the first place distilled at 150°, which removes the phosphorus oxychloride formed, the cyanuric chloride remaining with other products in the retort. The mixture in the retort is extracted with boiling dry ether, which, on evaporation, leaves crude cyanuric chloride. This must now be washed quickly with water, dried in a vacuum, and again extracted with ether. The ethereal solution thus obtained, when evaporated, gives the cyanuric chloride in crystals, which are readily identified by their melting point and characteristic odour.

III. *Hofmann's Test for Cyanuric Acid.*

This test is based on the characteristic property of cyanuric acid of giving a trisodium salt less soluble in warm than in cold concentrated solution of sodium hydroxide; I have applied it successfully in the case of all the specimens of the β-acid which I have prepared, even after the first recrystallisation.

IV. *Water of Crystallisation.*

Contrary to Herzig's experience, my specimens of the β-acid when purified by recrystallisation from water and dried by pressing between paper and subsequent exposure to the air for an hour, contain water which is given off below 120°, the proportion increasing with purification. The product of a fourth crystallisation gave the following percentage:—

Theory. $(C_3N_3)(OH)_3 2H_2O$.	Experiment.
21·8	15·8

The same specimen once more recrystallised retained a larger proportion of water. An experiment was made at the same time under precisely the same conditions with the ordinary acid, thus:—

Theory. $(C_3N_3)(OH)_3 2H_2O$.	Experiment, ordinary acid.	Experiment, β-acid.
21·8	21·9	19·7

It is clear then that the β-acid when purified does contain water of crystallisation, and that this is increased by purification, until, as seen in my last experiment, it amounts approximately to the two molecules contained in the crystals of the ordinary acid.

V. *Solubility in Alcohol.*

Herzig gives no determination of the solubility of the β-acid in alcohol. It is indeed, as he points out, more soluble in alcohol than the ordinary or the α-acid, but by successive recrystallisations its solubility is gradually reduced; thus:—

	1st crystallisation.	5th crystallisation.	6th crystallisation.
In 100 grams alcohol at 22—24°	0·425	0·240	0·156

This greater solubility, therefore, is due to the influence of some impurity which recrystallisation removes, and is not characteristic of the β-acid.

VI. *Barium Salt.*

Herzig did not succeed in preparing a definite barium salt from the β-acid. By carefully following the directions of Wöhler (*Annalen*, **62**, 252), however, I have obtained, as in the case of the α-acid, the monobarium compound in beautiful needles. It has the formula $(C_3N_3)(OH)_2(Oba) + H_2O$, which requires—

	Theory.	Experiment.
Barium	31·93	32·71

It thus appears that by simple recrystallisation from water "β-cyanuric" acid may be so purified that each of the properties which were supposed to distinguish it from the ordinary acid in turn disappears. By this means undoubtedly, small quantities of some impurity is taken away, which, although not sufficient to materially affect the analytical numbers as given by Herzig is, nevertheless, enough to modify in a remarkable manner the properties of the acid. β-cyanuric acid therefore, like the α-compound, is identical with ordinary cyanuric acid.

Chemical Laboratory,
University of Berlin,
July, 1886.

LXXI.—*The Constitution of Diazobenzeneanilide and its Relation to Amidoazobenzene.* II.

By R. J. Friswell and A. G. Green.

In a previous paper (Trans., 1885, 917) we have attempted to show that the isomeric change of diazobenzeneanilide (diazoamidobenzene) into amidoazobenzene, supposed to be brought about through the intervention of aniline hydrochloride, really consists in a splitting up of the molecule by the acid present into diazobenzene and aniline, and that these bodies again combine under the altered conditions with formation of amidoazobenzene. It appeared, however, necessary that the anilide should always be first formed, for under no conditions were we able to obtain a direct combination of diazobenzene and aniline to amidoazobenzene. This is most strikingly shown by the fact that the anilide can be produced at a temperature above 30° C. in the presence of a large excess of aniline hydrochloride or of aniline hydrochloride and aniline, although after standing for a short time it begins to change into the isomeride. Whilst on the other hand, pure diazobenzeneanilide free from aniline, if suspended in dilute hydrochloric acid (1 molecular proportion) is converted in the course of 24 hours at the ordinary temperature into amidoazobenzene hydrochloride, the liquor containing during the whole time some uncombined diazobenzenechloride.

The results obtained on continuing our experiments quite bear out our former conclusions, and we are now extending our investigation to

other diazoamides. The present paper chiefly deals with the constitution of diazobenzeneanilide, concerning which we believe we are able to advance some important evidence.

At the end of our former communication we suggested incidentally that the apparent analogy of diazobenzeneanilide to azoxybenzene was in favour of the symmetrical formula $\underset{\diagdown\ \diagup \atop NH}{C_6H_5{\cdot}N{-}N{\cdot}C_6H_5}$. In doing so we unintentionally somewhat misstated the views of Professor V. Meyer on this point, and now take the opportunity of correcting the error.

V. Meyer (*Ber.*, **14**, 2447, note to a paper by A. Sarauw), whilst admitting the symmetrical formula to be consistent with all the facts then known, yet does not regard it as altogether probable, and considers that the unsymmetrical formula $C_6H_5{\cdot}N_2{\cdot}NH{\cdot}C_6H_5$ will explain the facts equally well if a migratory power of the H-atom be assumed (brought about as he considers by addition and subtraction of HCl).

Contrary to our preconceived idea, our experiments have shown that the symmetrical formula is untenable, and that the analogy with azoxybenzene is only superficial. Although azobenzene is converted by sulphuric acid into oxyazobenzene, this isomeric change appears to be quite unlike the change of diazobenzeneanilide, for under no conditions of temperature or dilution could a trace of diazobenzene and phenol be detected. It also seemed possible that if diazobenzeneanilide had the symmetrical structure it might be produced from azobenzenedibromide, $C_6H_5{\cdot}\underset{Br}{N}{\cdot}\underset{Br}{N}{\cdot}C_6H_5$, by the action of ammonia: the dibromide seems to exist, although it is very unstable, but on passing dry ammonia into its solution in chloroform, azobenzene was regenerated.

A positive proof in favour of an unsymmetrical structure, $C_6H_5{\cdot}N_2{\cdot}NH{\cdot}C_6H_5$, was obtained by displacing the hydrogen of the imidogen-group by alcoholic radicles (the reaction taking place with extreme ease), and subsequently splitting up the product $C_6H_5{\cdot}N_2{\cdot}NRC_6H_5$ by an excess of acid.

A monoalkylated aniline was formed together with diazobenzene, the former of which could not have been obtained from a body of symmetrical structure. A similar proof was attempted some time ago by A. Sarauw (*Ber.*, **14**, 2443) by displacing the H-atom by CO by means of carbonyl chloride, but although his conclusions quite agree with ours, the results he obtained were very unsatisfactory and inconclusive, as from want of knowledge of the properties of diazobenzeneanilide, no precaution was taken to remove the hydrogen chloride

formed during the reaction; this must have acted on the anilide to produce diazobenzene, aniline, amidoazobenzene, tarry products, &c.

The symmetrical formula having been excluded, the only two remaining formulæ are:—

$$(a.)\ C_6H_5{\cdot}\underset{\displaystyle N}{\overset{}{\underset{|||}{N}}}{\cdot}NH{\cdot}C_6H_5. \qquad (b.)\ C_6H_5{\cdot}N{=\!=}N{\cdot}NH{\cdot}C_6H_5.$$

It might fairly be expected that a substance of the constitution (*a*) would when reduced allow the N-atom outside the chain to be removed in the form of ammonia, and that hydrazobenzene would be produced. Only alkaline reducing agents can be used, since acid reducing agents cause a preliminary decomposition into aniline and diazobenzene, the latter being then reduced to phenylhydrazine. We have tried the effect of various alkaline reducing agents, but the anilide is scarcely attacked by any. In one experiment we dissolved it in absolute alcohol and added a large excess of metallic sodium, a trace of ammonia was evolved, but the greater part of the anilide apparently remained unaltered, and hydrazobenzene was not formed.

Hence there seems little doubt that diazobenzeneanilide has the constitution $C_6H_5{\cdot}N{:}N{\cdot}NH{\cdot}C_6H_5$ usually attributed to it.

Diazobenzenemethylanilide (*Methyldiazoamidobenzene*), $C_6H_5{\cdot}N{:}N{\cdot}N(CH_3)C_6H_5$.

A solution of sodium ethoxide was prepared by dissolving 30 grams of clean sodium in 300 c.c. of absolute alcohol, and to this a hot solution of 200 grams of diazobenzeneanilide in 500 c.c. of absolute alcohol was added. The mixture was of a deep orange-brown colour; nothing separated from it when it was allowed to cool over lime in an exsiccator, but on exposure to the air it slowly absorbed water and diazobenzeneanilide separated in beautiful crystals.

When the solution was nearly cold, 170 grams of methyl iodide was added and the flask connected with an inverted condenser. A vigorous reaction quickly set in and the mixture boiled violently without the application of any external heat. After an hour's cohobation, half the alcohol was distilled off, and water was added to the residue; the heavy oily layer was separated, washed, and dried over calcium chloride. The product thus obtained was a dark-yellow, heavy oil which only became viscid in a freezing mixture and could not be caused to solidify by any treatment. It decomposed explosively when heated, and did not volatilise with steam, so that it could not be further purified. The yield of crude diazobenzenemethylanilide obtained was 200 grams.

Decomposition by Acid.—If the methylanilide is gently warmed with an excess of hydrochloric acid, diazobenzene can readily be detected in the solution, but is converted into phenol if the mixture is heated. 100 grams of the methylanilide was gradually added to 200 c.c. of hot strong hydrochloric acid: when the violent reaction was over, the solution was diluted with water, made strongly alkaline with caustic soda, and distilled. The crude methylaniline (yield 40 grams) was separated from the distillate, cohobated for some time with an alcoholic solution of carbon bisulphide and a little potash to remove a trace of aniline, separated and rectified. It boiled at 192—193° (uncorr.). Its platinochloride gave on analysis—

	Calculated for $(C_6H_5 \cdot NHMe,HCl)_2PtCl_4$.	Found. I.	II.	III.
Pt	31·52	31·11	31·19	31·32

The acetyl-derivative, obtained by heating the base with an equal weight of acetic anhydride, crystallised from water in beautiful, long, white needles having the constant melting point 101° (uncorr.). The melting point of methylacetanilide is given as 102°. The alkaline residue left after removing the methylaniline by distillation, contains phenol, which after acidifying was distilled off and isolated by adding salt to the distillate. It was identified by conversion into tribromophenol, $C_6H_2Br_3OH$, which crystallised from dilute alcohol in very fine, white needles, which had the correct melting point 96° (uncorr.).

Hence diazobenzenemethylanilide is decomposed by acids according to the equation—

$$C_6H_5 \cdot N : N \cdot NMeC_6H_5 + HCl = C_6H_5 \cdot N : N \cdot Cl + C_6H_5 \cdot NHMe.$$

Diazobenzenemethylanilide (1 mol.) when left in contact with cold dilute hydrochloric acid (1 mol.), is slowly converted in the course of 24 hours into a magma of small, dark crystals. This must consist for the most part of the hydrochloride of methylamidoazobenzene, but we have not yet succeeded in isolating this substance in a pure state, as it is very difficult to separate from a small quantity of amidoazobenzene which it appears to contain.

Diazobenzenebenzylanilide (*Benzyldiazoamidobenzene*),
$C_6H_5 \cdot N : N \cdot N(C_7H_7)C_6H_5$.

30 grams of sodium were dissolved in 300 c.c. of absolute alcohol, and a hot solution of 200 grams of diazobenzeneanilide in 500 c.c. of absolute alcohol was added. The mixture was cohobated for an hour or two with 140 grams of benzylchloride.

On adding water to the alcoholic solution the product was precipitated as an oil which was washed with hot water; on cooling it solidified.

After one crystallisation from alcohol it weighed 200 grams, which was diminished to 170 grams by a second crystallisation; it then melted at 80° (uncorr.). By further recrystallisation from a mixture of acetone and alcohol the melting point was raised to 81°, at which it remained constant. The pure benzylanilide forms beautiful yellow needles, very soluble in acetone, moderately soluble in alcohol, insoluble in water. A determination of the nitrogen by Dumas' method gave—

	Calculated for $C_{19}H_{14}N_3$.	Found.
N	14·63	14·87

The substance decomposes explosively on heating. When left in contact with 1 molecular proportion of dilute hydrochloric acid, slightly warm, it evidently undergoes change into the isomeric amidoazo-compound, but the benzylamidoazobenzene could not be isolated, as the product always separated as a tar.

Decomposition by Acids.—The diazobenzenebenzylanilide is resolved by an excess of acid into diazobenzene and benzylaniline. If the substance is gently warmed with strong hydrochloric acid diazobenzene can be readily detected in the solution, and phenol is obtained if the mixture is boiled.

50 grams of the benzylanilide was added by degrees to 200 c.c. of nearly boiling strong hydrochloric acid. Part of the benzylaniline hydrochloride separated at once and the rest crystallised out on cooling. The acid mother-liquor which contained the phenol was diluted with water and distilled, and the phenol was separated from the distillate by the addition of salt. It was identified as before by conversion into tribromophenol which melted correctly at 96° (uncorr.). The crude benzylaniline hydrochloride was treated with alkali and the product distilled. The base formed a pale yellowish, crystalline solid, which melted at 33° and boiled above 360° under ordinary pressure. The yield was about 20 grams.

The hydrochloride forms white plates melting at 203° (uncorr.); it is decomposed by water. On combustion with soda-lime it gave—

	Calculated for $(C_6H_5)(C_7H_7)NH,HCl$.	Found.
N	6·38	6·0

The platinochloride formed fine yellow needles melting at 168° (uncorr.), tolerably soluble in water. On analysis it gave—

	Calculated for $\{(C_6H_5)(C_7H_7)NH,HCl\}_2PtCl_4$.	Found.
Pt..............	25·23	25·14

Hence diazobenzenebenzylanilide is decomposed by acids according to the equation—

$$C_6H_5{\cdot}N:N{\cdot}N(C_7H_7)C_6H_5 + HCl = C_6H_5{\cdot}N:N{\cdot}Cl + (C_6H_5)(C_7H_7)NH.$$

We propose to prepare various other substituted derivatives of diazobenzeneanilide and of other diazoamides, and hope by applying this reaction to diazobenzeneparatoluide and paradiazotolueneanilide, $C_6H_5{\cdot}N_3H{\cdot}C_7H_7$, to prove whether these bodies are identical as at present assumed, and to determine their constitution. We hope also to investigate in the same manner the two compounds $\begin{array}{l}C_6H_4{\cdot}N_3H{\cdot}C_6H_5\\ |\\ C_6H_4{\cdot}N_3H{\cdot}C_6H_5\end{array}$, tetrazodiphenyldianilide and bidiazobenzenebenzidide, which according to our preliminary experiment do not appear to be identical.

In conclusion, we must express our thanks to the firm of Brooke, Simpson, and Spiller, Limited, in whose laboratories at the Atlas Works the above investigation was carried out.

LXXII.—COMMUNICATIONS FROM THE LABORATORY OF UNIVERSITY COLLEGE, BRISTOL.

I. *The Estimation of Free Oxygen in Water.*

By Miss KATHARINE J. WILLIAMS and Professor W. RAMSAY.

THE value of Schützenberger's method of determining the amount of free oxygen in water has been somewhat discredited by the verdict of those who have attempted to apply it; and in Sutton's *Handbook of Volumetric Analysis*, p. 229, the subject is briefly dismissed with the remark: "The method of Mohr of finding the oxidising power of weak alkaline solutions of oxygen upon ferrous compounds, and subsequent titration by permanganate, as also that of Schützenberger with sodic hyposulphite and ammoniacal copper solution, regulated by indigo, are by no means consonant with each other, nor with the accurate gasometric method of Bunsen."

It was with the object of arriving at some definite conclusion regarding the accuracy of this method that the experiments to be here described were undertaken; and it may be stated in advance that the

method, in our hands, has proved a quick, fairly reliable method, not difficult in execution.

Schützenberger's description of his process is to be found in the *Comptes rendus*, **75**, 879, and also in his work on fermentation (*International Scientific Series*, **20**, 108). We think it may prove of interest, before proceeding to describe our own experiments, briefly to recapitulate here the essential parts of the process as carried out by the author himself; and also the variations in the process suggested by others who have made use of it.

The fundamental reaction consists in the absorption of oxygen by sodium hyposulphite, $NaHSO_2$. This salt, however, need not be pure. It is easily prepared in an available condition by adding to a solution of hydrogen sodium sulphite, $NaHSO_3$, an excess of zinc-dust, allowing the mixture to stand in a corked flask for about five minutes, and then, when cool, adding excess of milk of lime, and filtering. The filtered solution may be kept under a layer of benzene in a stoppered bottle, and diluted as required. To standardise the sodium hyposulphite, an ammoniacal solution of copper sulphate, containing 4·46 grams of hydrated salt per litre, is employed. On adding the hyposulphite to the copper solution, the blue colour changes to yellow, the copper being reduced to the cuprous condition: 10 c.c. of the copper solution is equivalent to 1 c.c. of oxygen gas, measured at normal temperature and pressure. The titration is performed in an atmosphere of hydrogen.

A solution of indigocarmine is also employed, and its strength determined by titration with hyposulphite until the blue colour is destroyed.

Two methods of estimating oxygen were employed by Schützenberger. In the first, the water containing dissolved oxygen is placed in a Wolff's bottle, into which the burettes containing respectively indigo solution and sodium hyposulphite deliver; after the air has been displaced by hydrogen, indigo is added in small quantity so as to colour the liquid, and hyposulphite is then added until the colour is destroyed. In the second method, warm water is first placed in the Wolff's bottle, and about 40 c.c. of indigo is added. The liquid is then carefully decolorised by addition of hyposulphite. A known volume of the water to be tested is then introduced, the oxygen in which restores the colour of the indigo, partially oxidising it. The colour is again destroyed by addition of hyposulphite, the volume taken being noted, and from the volume of hyposulphite, of which the strength has been previously determined by means of the ammoniacal cupric solution, the percentage of free oxygen in the water is calculated. The first of these methods, Schützenberger states, estimates only half the oxygen in the water, and he suggests

that the remaining half combines with the water to form hydrogen peroxide. The second method is therefore in his opinion the only available one. On this point we shall have something to say hereafter.

A comparison of Schützenberger's method with Mohr's was next made by J. König and L. Mutschler (*Ber.*, **10**, 2017). The only difference between their method of experiment and Schützenberger's is a trivial one; they employed a more dilute solution of indigo. They give nine series of determinations, referring to water saturated with air, to ordinary well-water, and to water saturated with pure oxygen gas. Their first seven determinations show fair concordance between Mohr's method, which consists in the oxidation of ferrous to ferric salt, and Schützenberger's; but the two last, referring to water saturated with oxygen gas, are at variance with each other. In each case the hyposulphite method gave higher results; and they concluded therefore that Mohr's method is more trustworthy. They also agree with Schützenberger that hydrogen peroxide is produced during the addition of hyposulphite.

These conclusions were again confirmed by König alone (*Ber.*, 1880, 154).

F. Tiemann and C. Preusse published the results of their observations in the *Berichte*, **12**, 1768. Not only do they add the water to be tested to hot water, but they keep the liquid warm (about 40—45°) during the estimation. In every case three determinations were made before emptying their vessel, for they had no arrangement to syphon off the liquid without interfering with the current of hydrogen. They recommend that the solutions should be of such a strength that not more than 6 c.c. of hyposulphite is used to decolorise 10 c.c. of copper solution; and having once for all determined the ratio between copper and indigo, they do not subsequently standardise their hyposulphite against copper. They control their results by comparison with Mohr's method and also by expelling the gases by boiling the water to be tested, and estimating the oxygen by absorption. They conclude that Schützenberger's method gives results concordant with those obtained by gas analysis, whilst Mohr's method, in every case but one, gave results lower than either. They recommended Schützenberger's method for rapid work, but claim greater accuracy for the direct measurement of gaseous oxygen.

August Bernthsen (*Ber.*, **13**, 2277) again investigated this process. He employed pure sodium hyposulphite, considering it to give better results than the impure solution containing sodium sulphite. He quotes eight series of experiments, in which his copper solution was standardised against hyposulphite; and he employed

much stronger solutions of hyposulphite than Tiemann and Preusse recommended; indeed in one instance, only 2·65 c.c. of hyposulphite was required for 25 c.c. of copper solution. Some difficulty was experienced in detecting the true end-point, and the general verdict is unfavourable to the process. No examples as regards the application of the method to the estimation of free oxygen in water are given by him; his object was rather to test a process for the estimation of indigo.

On reviewing this evidence, it is on the whole not unfavourable to the process; and the results now to be given justify this conclusion.

The apparatus used by us closely resembled that recommended by Schützenberger. The reaction took place in a wide-mouthed glass bottle, closed by an india-rubber cork in which five holes had been bored. Through two of these passed the exit-tubes of burettes containing respectively indigo solution and hyposulphite, by means of the usual arrangement these burettes could be filled from stock-bottles from below by means of T-tubes. The third hole served to introduce the hydrogen from a continuous supply apparatus; the hydrogen having been purified by passing over stick potash and through sulphuric acid. Through the fourth hole, a doubly-bent tube was inserted, serving, when drawn up above the level of the liquid in the bottle, as an exit-tube for the hydrogen, and when pushed down, as a means of emptying the bottle. A tube provided with a stopcock, and connected with a reservoir, passed through the fifth hole, and was used in introducing the water to be tested into the bottle.

The hyposulphite solution was prepared by saturating a strong solution of 100 grams of sodium sulphite with sulphurous anhydride, adding 20 grams of zinc-dust, and cooling. Milk of lime, prepared from about 20 grams of quicklime was added, and the resulting solution was then transferred into the stock-bottle, which was fitted up like a wash-bottle, the liquid, however, being covered with a layer of benzene to exclude air. Such a solution is serviceable for at least two months. This solution was diluted for use until about 7 to 9 c.c. is equivalent to 10 c.c. of copper solution. The weak solution was kept in a bottle guarded from oxygen by a layer of benzene and by bulb-tubes full of potassium pyrogallate; from this the burette could be supplied from below as required. Before use, this solution was always standardised against copper solution or indigo.

The solution of copper was prepared according to Schützenberger's directions; the solution of indigo, however, recommended by him was found to be too strong to give good results. With a strong solution of indigo, the colour change is very difficult to detect. The most satisfactory results were obtained with a solution of indigo of such strength that 10 c.c. of hyposulphite was required to decolorise

20 c.c. Some experiments were made using warm water; but it was soon found that identical results were obtained, only after a somewhat longer time, at the ordinary temperature, and our experiments were therefore made without application of heat.

The experiments were conducted as follows:—Having expelled all air from the bottle by a current of hydrogen, the water to be tested was admitted through the bulb-tube; a few c.c. of indigo was added to tinge the water, and then hyposulphite was added from the burette until the blue colour changed to yellow. On standing for some minutes, it again changed to blue. More hyposulphite was added from time to time until the solution remained permanently yellow. The indigo having previously been compared with hyposulphite, the amount of the latter equivalent to the small quantity of indigo added was deducted from the total amount used; and the remainder was assumed to have reacted with the free oxygen in the water. This is the first method given by Schützenberger.

The other method employed was to add a considerable amount of indigo to about 100 c.c. of water in the bottle, and to destroy its colour with hyposulphite. The water to be tested was then added, and the resulting blue colour again destroyed. In this case the amount of oxygen is calculable directly from the amount of hyposulphite taken.

Results.

We first give instances of the application of Methods I and II, with full details, so that some idea may be gained as to the concordance of the individual results with each other.

1. Standardising solutions:—

Sodium hyposulphite and copper solution.		Hyposulphite and indigo solution.	
Copper solution taken.	Hyposulphite used.	Indigo taken.	Hyposulphite used.
10 c.c.	9·31 c.c.	6 c.c.	1·34 c.c.
10 „	9·26 „	6 „	1·50 „
10 „	9·39 „	6 „	1·52 „
10 „	9·40 „	6 „	1·40 „
10 „	9·36 „	Mean 6 „	1·44 „
Mean 10 „	9·34 „		

And 10 c.c. indigo require 2·4 c.c. hyposulphite.

2. Determinations of free oxygen in water, according to Method I. This shows the first stage. It is not always easy to stop accurately when the first reaction is complete, hence the less concordance of the results of the different series. The water used was ordinary Bristol tap-water, shaken with air.

Series I:—

Water taken.	Indigo.	Total hyposulphite.	Hyposulphite used for oxygen.
300 c.c.	4 c.c.	9·73—1·00	8·73 c.c.
,,	4 ,,	9·96—1·00	8·96 ,,
,,	4·25 c.c.	9·78—1·06	8·72 ,,
,,	4 c.c.	9·87—1·00	8·87 ,,
		Mean	8·82 c.c.

The strength of the solution of indigocarmine was such that it required 1 c.c. of hyposulphite to decolorise 4 c.c. of indigo. 1000 c.c. of water from the above results would require 29·4 c.c. of the hyposulphite; and as 9·41 c.c. of hyposulphite was equivalent to 10 c.c. of copper solution, each c.c. of copper solution being equivalent to 1 c.c. of oxygen at normal temperature and pressure, the total amount of oxygen per litre is 3·124 c.c.

Series II, III, and IV, Bristol tap-water, shaken with air. The equivalent of the added indigo in hyposulphite has been subtracted.

Water taken.	Hyposulphite used for oxygen. II.	III.	IV.
250 c.c.	6·28 c.c.	8·08 c.c.	7·83 c.c.
,,	6·20 ,,	8·06 ,,	7·74 ,,
,,	6·01 ,,	8·01 ,,	—
,,	—	8·18 ,,	—
Mean	6·16 c.c.	8·08 c.c.	7·78 c.c.

Series II. 7·397 c.c. $NaHSO_2$ = 10 c.c. copper solution. 1000 c.c. water required 24·64 c.c. $NaHSO_2$; therefore free oxygen = 3·331 c.c.

Series III. 8·94 c.c. $NaHSO_2$ = 10 c.c. copper solution. 1000 c.c. water required 32·32 c.c. $NaHSO_2$; therefore free oxygen = 3·619 c.c.

Series IV. 9·34 c.c. $NaHSO_2$ = 10 c.c. copper solution. 1000 c.c. water required 31·12 c.c. $NaHSO_2$; therefore free oxygen = 3·112 c.c.

Second stage of Method I.

Bristol tap-water shaken with air was again employed. Series I, II, and III.

Water taken.	Hyposulphite used for oxygen. I.	II.	III.
250 c.c.	12·72 c.c.	10·27 c.c.	9·92 c.c.
,,	12·43 ,,	10·36 ,,	9·70 ,,
,,	12·64 ,,	10·52 ,,	10·04 ,,
,,	12·45 ,,	10·05 ,,	—
,,	12·75 ,,	—	—
Mean	12·598	10·30	9·88 c.c.

Series I. 9·34 c.c. $NaHSO_2$ = 10 c.c. copper solution. 1000 c.c. water required 50·232 c.c. $NaHSO_2$; therefore free oxygen = 5·371 c.c.

Series II. 7·397 c.c. $NaHSO_2$ = 10 c.c. copper solution. 1000 c.c. water required 41·20 c.c. $NaHSO_2$; therefore free oxygen = 5·570 c.c.

Series III. 7·21 c.c. $NaHSO_2$ = 10 c.c. copper solution. 1000 c.c. water required 39·52 c.c. $NaHSO_2$; therefore free oxygen = 5·480 c.c.

3. Method II. The following results were obtained with Bristol tap-water shaken with air.

Series I and II.

Water taken.	Hyposulphite used to decolorise indigo. I.	II.
100 c.c.	5·06	3·86
,,	5·11	3·68
,,	5·20	3·62
,, }	10·81	{ 3·69
,, }		{ 3·97
,,	—	3·82
Mean	5·236	3·77

Series I. 9·41 c.c. $NaHSO_2$ = 10 c.c. copper solution. 1000 c.c. water required 52·36 c.c. $NaHSO_2$; therefore free oxygen = 5·564 c.c.

Series II. 7·21 c.c. $NaHSO_2$ = 13 c.c. copper solution. 1000 c.c. water required 37·7 c.c. $NaHSO_2$; therefore free oxygen = 5·229 c.c.

It will be seen that the first method gave, when pushed to its last stage, as a mean result of three series ,5·474 c.c. of oxygen per litre;

this number agrees well with that obtained by the second method, as a mean of two series, 5·396 c.c.

It appeared desirable to check these numbers by a direct measurement by gas analysis of the total oxygen expellable from water by boiling. The carbonic anhydride was removed with caustic potash, and the oxygen with cuprous chloride. The following results were obtained with Bristol water shaken with air:—

1. Free oxygen....	5·63 c.c.	Mean 5·402 c.c.
2. Free oxygen....	5·26 ,,	
3. Free oxygen....	5·454 ,,	
4. Free oxygen....	5·263 ,,	

Mean of other methods, 5·435 c.c. It is thus seen that Schützenberger's method may be regarded as a fairly accurate process for determining free oxygen in water, whichever way be adopted for its determination.

It was suggested by Schützenberger, that the discrepant results obtained by his first and by his second methods depended on the formation of peroxide of hydrogen; he stated that only half the oxygen was estimated by the first method, and he accounted for this by the supposition that the remaining half of the oxygen was converted into hydrogen peroxide. König (*Ber.*, **13**, 154), on comparing Mohr's and Schützenberger's processes, found too high results by the former; he supposed that the discrepancy was caused by the presence of hydrogen peroxide, which, he stated, acts on ferrous sulphate, but not on sodium hyposulphite.

Now it will be seen, on comparing our results by Schützenberger's first and second methods, that the mean result of four series of experiments with the first, is 3·2961 c.c. of free oxygen, or rejecting the third series which gave high results, 3·189 c.c.; and on taking the ratios of the mean of Method I to that of Method II, the number 1·66 is obtained; or if Series III be rejected, 1·7. It is therefore clear that the ratio of the oxygen estimated by the first half of the first method to the total oxygen is not, as stated by Schützenberger, 1 : 2, but 3 : 5, approximately. But it is difficult to devise an equation which will in a rational manner account for this partition of oxygen. It may possibly be caused by some partition between indigo and hyposulphite, for which the conditions of temperature and dilution were favourable to the proportion found.

In spite of Schützenberger's statement, for which there appeared little foundation, that hydrogen peroxide is not attacked by sodium hyposulphite, we thought the experiment worth a trial. König also confirms Schützenberger's remark, but our results do not bear out their conclusions.

A dilute solution of hydrogen peroxide was prepared, and standardised with weak potassium permanganate containing 2·661 grams per litre. Although hydrogen peroxide is heavier than water, yet such a dilute solution has so nearly the same specific gravity that the difference may be neglected. The mean of four very concordant estimations proved that the solution of peroxide contained available oxygen equal to 221·4 c.c. per litre. It was immediately tested with hyposulphite by Method I, with the results which follow :—

Solution of peroxide taken.	Hyposulphite employed.
100 c.c.	6·75 c.c.
"	6·84 "
"	7·00 "
Mean	6·86 c.c.

9·41 c.c. of $NaHSO_2$ = 100 c.c. of copper solution. 1000 c.c. of peroxide solution required 68·6 c.c. of $NaHSO_2$; therefore oxygen estimated = 7·28 c.c.

On standing for some minutes, however, the solution again regained its colour, and required further addition of 13·59 c.c. of hyposulphite before a permanent discharge of colour was produced. This is equivalent to a total of 204·5 c.c. per litre, and oxygen estimated = 20·67 c.c.

The same solution of peroxide was then tested by Method II.

Solution of peroxide taken.	Hyposulphite employed.
100 c.c.	18·99 c.c.
"	18·39 "
"	18·58 "
Mean	18·68 c.c.

4·87 c.c. $NaHSO_2$ = 10 c.c. of copper solution. 1000 c.c. of peroxide solution required 186·8 c.c. of $NaHSO_2$; therefore oxygen estimated = 38·36 c.c.

A fresh solution of peroxide was prepared, and as a mean of five very concordant estimations with potassium permanganate, was found to contain available oxygen equal to 213·76 c.c. per litre. The same solution was tested with potassium iodide and sodium thiosulphate, and was found to contain 214·06 c.c. of available oxygen per litre. It was titrated with hyposulphite by both methods, with the following results :—

Solution of peroxide taken.	Method I. Intermediate stage.	Method I. Final stage.	Method II.
100 c.c.	6·71 c.c.	17·93 c.c.	37·01 c.c.
,,	6·53 ,,	18·23 ,,	36·73 ,,
,,	—	18·04 ,,	40·39 ,,
,,	6·16 ,,	17·90 ,,	—
Mean	6·46 c.c.	18·02 c.c.	38·04 c.c.

8·78 c.c. $NaHSO_2$ = 10 c.c. copper solution. 1000 c.c. of peroxide solution required for intermediate stage, 64·6 c.c. of $NaHSO_2$ = 7·35 c.c. of free oxygen; and in final stage, 180·2 c.c. of $NaHSO_2$ = 20·52 c.c. of free oxygen.

By Method II, 1000 c.c. required 380·4 c.c. = 43·20 c.c. of free oxygen.

A third solution of peroxide was prepared, and contained available oxygen equal to 159·06 c.c. per litre. Two estimations by Method I showed that in the final stage 15·03 c.c. of this oxygen was extracted. After standing all night, this amount was increased to 16·60 c.c.

These determinations show that peroxide is partially estimated by hyposulphite. The strength of the first and second samples of peroxide was nearly the same, and the results by Methods I are nearly identical. But the third sample of peroxide was more dilute, and appears therefore to be more stable. It is noticeable that the results by Method I pushed to its concluding stage, and by Method II, are here by no means identical. We have here also, doubtless, an instance of partition of oxygen between indigo-white and hyposulphite, constant for the particular dilution and temperature employed. It may also be concluded that on diluting hydrogen peroxide with water some decomposition takes place, for after standing over night, the amount of free (or available?) oxygen had slightly increased.

It seemed to us that it might be interesting to ascertain the loss of oxygen suffered by water on boiling briskly. This was suggested by the very great difficulty experienced by one of us in expelling all the air from water by boiling, even in a vacuum.

After boiling for half-an-hour, Bristol tap-water contained still 2·09 c.c. of free oxygen per litre; and after an hour's boiling, the amount was still 0·45 c.c. When frozen by evaporation by a Carré's pump, and then thawed, the water still contained 1·95 c.c. of free oxygen per litre. These experiments show how difficult it is to remove oxygen gas from water.

In conclusion, we would state that we are confident that the process of estimating oxygen, recommended by Schützenberger, is fairly accurate and rapid; and that both methods described by him give

identical results, when the reactions are allowed to reach their final stage. The second is the more rapid, and is consequently preferable.

Addendum.—Since writing the above, our attention has been drawn to a paper by Dr. Dupré, published in the *Analyst*, 11, 156. We agree with him that the estimation of free oxygen in a sample of water, saturated with air, forms a reliable method for standardising the hyposulphite solution. We cannot, however, agree with him in his conclusion that when Schützenberger's first method is used, the end-point of the first reaction indicates that exactly half the oxygen in the water has been estimated. Dr. Dupré gives no analytical details to confirm this statement; and those adduced by us in the foregoing paper show conclusively, we think, that the hyposulphite required for the partial reaction does not bear to that required for the completed reaction the proportion 1 : 2, but 3 : 5. Our experiments, however, bear out Dr. Dupré's, in the more important conclusion that the final stage of Method I gives results identical with those of Method II.

LXXIII.—*Determinations of Vapour-pressures of Alcohols and Organic Acids, and the Relations existing between the Vapour-pressures of the Alcohols and Organic Acids.*

By ARTHUR RICHARDSON, Ph.D., University College, Bristol.

Apparatus Used.—The vapour-pressures of the alcohols and acids were determined by means of the apparatus described by Drs. Ramsay and Young (*Chem. Soc. Trans.*, 1885, 42). The following alcohols and acids were examined:—

Methyl Alcohol, obtained from Kahlbaum as free from acetone, was distilled after standing 24 hours over calcium oxide, the last traces of water being then removed by treatment with small quantities of metallic sodium and subsequent distillation. It boiled at 65·8° at 760 mm.

Ethyl Alcohol.—A nearly pure specimen was provided by Dr. Ramsay, the last traces of water being removed by distillation after treatment with metallic sodium. It boiled at 78·2° at 760 mm.

Normal Propyl Alcohol (pure from Kahlbaum) was distilled after treatment with metallic sodium, as in the previous cases; the fraction which distilled over at 97·2° at 746·4 mm. was taken as pure.

Experimental Results.

The numbers representing the vapour-pressures of the alcohols and acids at different temperatures are given in the following tables; in all cases two series of experiments were made for each substance in order to check the results obtained.

Vapour-pressures.

Methyl alcohol.				Ethyl alcohol.			
1st experiment.		2nd experiment.		1st experiment.		2nd experiment.	
Temp. in C.°	Pressure in mm.	Temp. in C.°	Pressure in mm.	Temp. in C.°	Pressure in mm.	Temp. in C.°	Pressure in mm.
− 8·3	17·3	− 10·1	15·05	4·2	16·89	− 3·3	10·23
− 7·3	19·2	− 7·3	18·32	4·8	17·94	+ 7·3	22·39
− 3·3	24·33	− 6·3	19·09	8·8	23·31	13·6	30·67
− 2·3	25·23	− 6·3	19·44	9·8	24·51	19·8	45·22
+ 0 7	32·06	− 5·3	21·24	10·7	25·80	23·5	56·25
2·2	35·15	− 4·8	20·54	17·2	38·57	26·8	68·96
4·2	38·30	− 1·7	26·92	21·8	50·72	29·6	80·61
6·25	43·88	+ 0·2	28·67	22·6	51·96	30·7	83·86
8·5	48·97	4·7	36·89	23·1	54·86	32·8	95·10
11·2	55·82	7·7	48·87	25·3	62·48	34·8	104·81
12·0	59·84	12·2	58·48	27·3	71·11	37·3	119·97
16·7	77·99	14·7	68·72	30·7	81·86	42·2	155·59
22·7	108·96	20·7	94·03	35·3	107·22	43·8	165·41
27·3	133·55	23·7	112·19	36·6	114·59	46·5	189·56
30 2	155·34	25·7	124·85	40·1	138·41	50·05	226·99
33·3	183·77	31·7	158·07	43·1	162·96	52·8	257·52
39·2	235·13	36·2	202·83	47·2	199·18	55·50	258·49
43·7	289·84	46·6	332·37	49·6	222·87	59·80	349·02
49·2	370·26	54·7	459·22	53·7	269·83	65·80	451·48
56·7	500·20	58·7	552·47	57·3	320·87	68·80	513·76
59·9	584·24	66·45	754·9	61·0	370·12	71·10	569·64
65·7	753·05	—	—	—	—	73·80	642·98

Isobutyl Alcohol, supplied pure from Kahlbaum, was fractionated; after treatment with sodium the greater portion passed over at 107·7° at 755 mm.; this fraction was used.

Isoamyl Alcohol.—A sample, provided by Dr. Ramsay, was fractionated; after treatment with sodium that portion boiling constantly at 130·1° at 760 mm. was taken as pure (p. 764).

Glycerol.—A sample was taken, distilled in a vacuum, and the distillate collected when the boiling point was constant; this portion was considered free from water.

Formic Acid, obtained from Kahlbaum, was distilled, and the fraction which boiled constantly at 101·3° at 760 mm. was used.

Acetic Acid.—A pure specimen was provided by Dr. Ramsay. It boiled at 118·5° at 760 mm. (p. 765).

Propionic Acid.—A specimen obtained from Kahlbaum was fractionated, and the distillate which passed over at 140·3° at 760 mm. was taken as pure.

Isobutyric Acid was fractionated, and the portion which boiled constantly at 153° at 760 mm. was used (p. 766).

Isovaleric Acid.—An aqueous solution was distilled, and the fraction boiling above 150° was repeatedly shaken with phosphoric pentoxide; on again distilling, the greater portion passed over at 174·9° at 750 mm.; this fraction was taken as pure (p. 767).

Vapour-pressures—continued.

Normal propyl alcohol.				Isobutyl alcohol.			
1st experiment.		2nd experiment.		1st experiment.		2nd experiment.	
Temp. in C°.	Pressure in mm.	Temp. in C°.	Pressure in mm.	Temp. in C°.	Pressure in mm.	Temp. in C°.	Pressure in mm.
11·45	8·56	1·7	4·59	32·8	18·44	25·3	11·212
14·9	10·96	2·3	4·59	46·8	42·92	35·4	21·426
23·7	18·82	4·8	5·19	52·8	62·68	37·9	26·160
28·2	24·96	6·2	5·78	57·8	88·76	42·0	33·123
33·8	34·90	10·8	7·84	61·3	98·68	46·7	44·069
35·1	39·81	11·7	8·83	66·0	116·29	50·8	55·666
36·7	40·67	13·2	9·49	67·75	134·85	54·9	71·61
38·2	45·50	13·7	9·49	69·9	151·20	58·8	85·86
39·2	47·40	20·7	15·46	74·8	194·68	62·3	103·043
41·7	54·88	30·6	29·04	77·2	213·77	65·8	123·920
44·7	65·21	33·7	35·23	78·7	226·82	66·0	124·617
48·1	84·32	36·7	40·81	80·55	244·61	68·8	134·110
53·9	106·92	43·7	61·67	81·0	259·56	71·8	166·62
55·7	119·25	46·7	73·50	83·6	284·30	73·8	182·38
56·5	129·23	48·7	83·53	85·3	304·47	75·9	204·09
59·7	143·0	75·2	300·67	87·3	332·32	78·7	229·45
62·5	163·96	81·9	400·67	90·3	378·12	81·3	259·001
66·2	214·75	94·1	711·01	92·8	418·12	84·8	297·587
68·7	220·74	97·2	746·45	95·8	478·117	87·8	347·467
74·5	287·3	—	—	98·05	524·86	91·55	399·35
79·2	358·75	—	—	101·55	593·86	92·95	428·94
85·7	477·51	—	—	102·75	626·264	95·40	468·978
90·2	566·22	—	—	104·8	669·113	96·80	527·363
97·2	745·45	—	—	105·8	708·36	100·7	575·651
—	—	—	—	—	—	102·8	630·890
—	—	—	—	—	—	104·8	680·830
—	—	—	—	—	—	107·7	755·114

Vapour-pressures—continued.

Isoamyl alcohol.				Glycerol.			
1st experiment.		2nd experiment.		1st experiment.		2nd experiment.	
Temp. in C°.	Pressure in mm.	Temp. in C°.	Pressure in mm.	Temp. in C°.	Pressure in mm.	Temp. in C°.	Pressure in mm.
34·7	7·27	35·8	6·896	118·45	0·238	122·8	0·597
41·9	9·97	46·5	14·0	118·75	0·298	127·91	0·746
53·8	21·87	47·8	15·67	120·77	0·348	135·51	1·165
66·68	46·58	58·3	29·34	122·92	0·398	136·52	2·340
72·80	63·93	65·55	42·853	123·85	0·448	145·555	3·285
77·65	82·87	67·8	48·16	127·91	0·4978	152·34	4·659
84·40	116·60	70·3	56·56	130·8	1·891	163·36	7·417
90·55	150·98	73·0	65·46	134·8	1·941	169·70	12·059
91·90	164·93	74·25	69·613	137·025	2·00	175·52	15·683
92·30	167·92	76·8	79·06	138·39	2·191	183·40	20·512
95·65	193·08	78·05	85·66	139·04	2·338	192·0	30·62
96·80	196·07	81·55	100·04	141·04	2·588	199·8	41·81
103·80	276·15	82·05	102·548	141·04	2·387	205·8	52·767
104·0	279·04	84·9	107·18	143·645	3·046	211·55	68·703
107·0	314·72	85·8	113·609	147·06	3·385	217·3	86·725
107·70	319·71	88·95	143·0	151·99	4·083	224·3	115·25
109·30	345·96	89·55	145·5	161·25	6·527	227·0	130·535
111·50	387·0	90·6	155·56	162·45	8·115	229·8	144·87
111·80	388·67	93·7	175·87	171·05	12·694	237·1	183·503
112·80	399·80	95·65	190·41	172·80	12·745	246·4	239·95
115·80	452·20	99·20	220·60	183·25	20·461	248·5	258·627
118·80	524·21	101·80	253·59	195·30	34·369	245·3	266·85
120·80	536·81	103·7	273·52	200·8	44·865	257·3	347·092
123·50	598·40	106·8	304·74	201·3	45·61	—	—
124·80	628·92	108·8	334·42	211·5	65·61	—	—
128·55	681·46	110·9	370·44	220·3	100·813	—	—
—	—	114·3	417·7	229·5	137·95	—	—
—	—	121·1	524·36	241·80	201·225	—	—
—	—	123·6	591·75	250·3	231·872	—	—
—	—	—	—	260·4	385·326	—	—

Vapour-pressures—continued.

Formic Acid.

1st experiment. Temp. in C°.	1st experiment. Pressure in mm.	2nd experiment. Temp. in C°.	2nd experiment. Pressure in mm.
55·9	151·9	18·5	28·657
61·1	185·39	22·7	34·588
68·7	245·2	29·7	47·844
76·2	318·72	39·1	73·262
82·7	391·23	44·45	82·97
87·7	467·47	57·3	156·89
91·2	529·03	64·9	207·423
92:7	562·17	68·6	238·22
96·6	648·89	71·7	276·90
97·9	677·76	75·2	310·088
100·45	728·43	—	—
101·7	762·52	—	—

3rd experiment.

Temp. in C°.	Pressure in mm.
5·7	13·46
6·1	14·60
7·2	13·46
10·2	17·44
13·2	20·93
21·7	32·94
29·7	48·33
35·7	65·02
44·3	84·82
46·2	99·165
57·2	152·96

Acetic Acid.

1st experiment. Temp. in C°.	1st experiment. Pressure in mm.	2nd experiment. Temp. in C°.	2nd experiment. Pressure in mm.
2·72	4·0	5·59	4·9
7·06	5·25	6·11	5·0
10·60	6·50	6·87	5·10
15·5	9·10	7·62	5·50
20·1	12·00	8·27	5·90
31·3	21·80	9·70	6·20
36·1	28·30	10·7	6·75
40·1	34·30	14·72	8·50
48·5	51·70	17·00	9·75
57·4	78·70	25·60	15·95
59·6	87·60	—	—
68·5	127·50	—	—
69·1	131·90	—	—
73·2	156·20	—	—
81·65	215·20	—	—
91·4	307·90	—	—
100·6	425·20	—	—
105·45	501·80	—	—
110·4	587·10	—	—
114·1	657·50	—	—
117·15	717·90	—	—
—	—	—	—
—	—	—	—
—	—	—	—
—	—	—	—
—	—	—	—
—	—	—	—
—	—	—	—
—	—	—	—
—	—	—	—
—	—	—	—
—	—	—	—

Vapour-pressures—continued.

Propionic acid.				Isobutyric acid.			
1st experiment.		2nd experiment.		1st experiment.		2nd experiment.	
Temp. in C.°	Pressure in mm.	Temp. in C.°	Pressure in mm.	Temp. in C.°	Pressure in mm.	Temp. in C.°	Pressure in mm.
15·45	2·74	13·9	2·49	23·8	0·996	44·05	5·873
16·2	2·74	14·7	2·98	32·6	2·097	48·55	7·366
20·2	2·99	16·7	3·587	32·6	2·193	67·20	20·90
28·7	4·73	20·45	3·98	34·55	2·798	70·60	24·73
31·7	5·48	24·7	4·98	37·55	3·584	85·80	53·25
31·7	5·48	49·6	15·84	38·8	3·787	92·30	72·71
35·7	6·97	56·2	21·92	51·8	12·158	98·80	97·79
39·7	8·37	60·12	19·44	64·8	18·436	104·80	127·90
46·7	13·20	65·2	35·87	76·4	34·78	110·30	160·00
55·0	22·02	81·2	76·73	83·8	51·07	115·80	205·29
69·7	43·85	92·7	131·34	89·8	66·369	123·00	279·04
77·7	66·27	103·2	196·56	96·3	89·09	126·80	308·57
83·2	86·45	117·7	338·08	103·8	129·75	131·20	358·84
87·7	104·139	135·7	649·74	107·3	147·09	136·05	411·19
100·7	176·39	—	—	111·8	177·237	143·80	552·24
108·7	247·89	—	—	119·3	236·03	153·3	761·27
113·7	303·44	—	—	124·3	283·66	—	—
120·3	388·80	—	—	130·55	358·76	—	—
125·45	453·50	—	—	133·80	406·59	—	—
132·7	572·25	—	—	135·55	451·03	—	—
135·7	650·00	—	—	139·80	522·03	—	—
140·3	760·0	—	—	143·80	601·49	—	—

Vapour-pressures—continued.

Isovaleric acid.

1st experiment.		2nd experiment.		3rd experiment.	
Temp. in C.°	Pressure in mm.	Temp. in C.°	Pressure in mm.	Temp. in C.°	Pressure in mm.
51·3	2·588	51·79	2·741	55·4	3·388
59·4	3·635	56·25	3·335	73·51	10·714
60·8	4·678	58·74	3·932	88·85	23·99
69·9	8·212	62·725	4·977	96·10	34·88
88·2	22·891	65·45	5·725	106·22	58·149
92·9	28·468	73·51	9·955	111·36	62·588
102·4	46·982	84·12	18·914	115·42	80·727
107·8	56·225	89·35	24·291	123·85	122·595
111·8	74·354	92·51	28·372	130·0	154·785
120·55	104·96	93·32	29·867	133·01	174·01
124·4	125·71	93·82	31·087	135·02	185·552
128·8	155·873	96·81	35·977	138·04	218·262
130·9	186·929	101·38	42·45	142·25	253·443
136·4	212·014	106·275	55·891	146·36	292·310
140·0	264·05	112·09	63·805	151·29	349·716
145·8	299·31	112·62	72·273	155·01	399·95
151·8	370·674	114·65	81·482	155·11	398·611
155·8	436·72	116·70	88·799	157·20	434·53
157·6	479·06	124·05	122·298	158·26	440·91
161·3	557·0	133·0	175·159	163·45	526·52
173·3	645·19	138·25	218·114	171·15	673·23
—	—	143·05	256·192	174·93	744·99
—	—	148·67	312·085	—	—
—	—	150·3	368·386	—	—
—	—	153·1	369·531	—	—
—	—	158·27	434·039	—	—
—	—	162·4	492·774	—	—
—	—	165·625	551·877	—	—
—	—	171·25	673·252	—	—
—	—	176·0	745·587	—	—

From the construction of the apparatus used for making the vapour-pressure determinations, it is obvious that errors arising from the vapour becoming superheated are entirely avoided, for even if the vapours should become superheated, the liquid in contact with the thermometer bulb must be at the true boiling point, since it has a free surface of evaporation; that the temperature was sufficiently high was insured by keeping the temperature of the bath at least 30° higher than that of the evaporating liquid. The numbers given also represent the true vapour-pressures of the substances experimented on, for it has been shown by Regnault and others that the statical and

dynamical methods of measuring vapour-pressures give identical results; as, however, this identity has been denied by Kahlbaum (*Siedetemperatur und Druck*, Leipzig, 1885), the vapour-pressures of methyl and ethyl alcohol as obtained by the two methods are compared in the following table:—

Mm.	Methyl alcohol.		Ethyl alcohol.	
	Regnault.	Richardson.	Regnault.	Richardson.
50............	10° C.	9° C.	22·2° C.	21·8° C.
100............	22·45	21·8	34·8	34·0
150............	30·2	30·0	42·2	41·8
200............	36·0	35·9	48·0	47·4
250............	40·9	40·5	52·6	52·2
300............	44·7	54·4	56·6	56·0
350............	48·0	47·9	60·0	59·5
400............	51·1	51·0	62·7	62·5
450	54·0	54·4	65·9	65·5
500............	56·8	56·5	68·5	68·3
550............	58·8	58·5	70·3	70·0

The vapour-pressures of some of the acids of the acetic series have been determined by Landolt (*Annalen*, Sup. 6, 129), but I believe his results are untrustworthy for the following reasons:—

(1.) In the case of the higher acids, the observed boiling points do not agree with those calculated from his formulæ; for example:, Butyric acid; observed boiling point 163° at 765·3 mm.; calculated 160·8° at 760 mm. Valeric acid; observed boiling point 175·6° to 176·1° at 766·2 mm.; calculated 173·7° at 760 mm.

(2.) In no case does Landolt appear to have boiled the mercury in his barometer tube; unless this is done it is impossible to insure absence of air in the tubes filled by such a method as he adopted. Landolt believed that errors due to this cause were eliminated by filling both the barometer and the experimental tubes in precisely the same way; it is extremely probable, however, that air adhering to the glass in the experimental tube would be carried up by the liquid as it rose through the mercury on being introduced from below, whereas in the barometer tube the air would remain for the most part adhering to the sides of the tube.

(3.) If Landolt's results for valeric acid are closely examined it will be seen—

(*a.*) That the boiling points of the two samples which he employed were almost identical.

(*b.*) That the vapour-pressures of the two samples at 40° were

respectively 18·9 mm. and 12 mm., corresponding to a temperature difference of about 14°.

(*c.*) That the vapour-pressures at 178·2° (slightly above the boiling point) differed in the two samples by 49·5 mm., equivalent to a difference in temperature of about 2°.

Now it has been proved that vapour-pressure determinations by the dynamical and statical methods are identical when the substance under examination is pure, and the fact that the boiling points of Landolt's two samples were almost identical whilst the vapour-pressures at the boiling points were widely different, can only be explained in one of two ways, either the substances were impure, or the determinations of the vapour-pressures were inaccurate (this remark applies to 1).

(4.) It has been shown with more than 50 substances that, when compared with water, the value C in the equation $R' = R + C(t' - t)$ is a constant through wide limits of pressure; the only observed exceptions are mercury, as determined by Regnault, and acetic, propionic, butyric, and valeric acids, as determined by Landolt; owing to this apparent anomaly in the case of mercury and to the unsatisfactory nature of Regnault's experiments with this substance, the vapour-pressures of mercury have been redetermined by Ramsay and Young, who find that mercury does not really form an exception to the above law. If the vapour-pressures of the acids given in this paper are correct, then these substances also conform to the law, whereas if Landolt's results are correct they are the only known exceptions to it.

Observed Relations between the Vapour-pressures of the Alcohols and Acids.

These substances were compared amongst themselves in order to ascertain whether a relation existed between them similar to that observed by Ramsay and Young (*Phil. Mag.*, Dec., 1885) between chlorobenzene and bromobenzene and between chloride and bromide of ethyl and other nearly allied compounds, where it was shown that the ratios of the absolute temperatures corresponding to equal vapour-pressures remain constant for very wide ranges of vapour-pressure. The acids and alcohols were also considered with reference to the further relation which exists between compounds not necessarily allied in properties and composition, for Ramsay and Young have shown that the ratios of the absolute temperatures of any two substances corresponding to an equal vapour-pressure are either constant for all vapour-pressures, or else the ratios increase or decrease with rise in temperature by an amount which is directly proportional to the rise in temperature.

In the subjoined table, the ratios of the absolute temperature of the

alcohols and acids are given for vapour-pressures between 50 mm. and 750 mm. It will be seen that in the case of methyl and ethyl alcohol, the ratio of the absolute temperature at 50 mm. is 1 : 1·045, diminishing with increased vapour-pressure to 1 : 1·035 at 700 mm.; a decrease is observed in the value of the ratios between ethyl and propyl alcohol from 1 : 1·062 to 1 : 1·051. In the case of propyl and isobutyl alcohol, however, the variation is much smaller, the ratio at 50 mm. being 1 : 1·027, at 700 mm. 1 : 1·029, whilst the value of the ratio of isobutyl and isoamyl alcohol is practically a constant for all vapour-pressures between 50 mm. and 750 mm.

Similarly the ratios of the absolute temperatures of formic acid and acetic acid vary considerably, being at low vapour-pressures 1 : 1·059, falling as the pressure rises to 1 : 1·049; so also with acetic and propionic acids, a fall in ratio from 1 : 1·071 to 1 : 1·054, accompanies the rise in vapour-pressure. On ascending the series, propionic and isobutyric acids are much more nearly constant in the values of their ratios at different vapour-pressures, being at 50 mm. 1 : 1·030, and at 750 mm. 1 : 1·037, the value of the ratios approaching a constant for all vapour-pressures between 50 mm. and 750 mm., in the case of isobutyric and isovaleric acids.

It would appear, therefore—

(1.) That the ratios of the absolute temperatures of the lower alcohols and acids diminish with increased vapour-pressure.

(2.) That among the higher alcohols and acids in the series the value of the ratios tends to become a constant number for vapour-pressures between 50 mm. and 750 mm.

Comparison of the Ratio of the Absolute Temperature of Alcohols and Acids for Vapour-pressures between 50 and 750 mm.

	Alcohols.								Acids.	
Mm.	$CH_3\cdot OH$ to	$C_2H_5\cdot OH$.	$C_2H_5\cdot OH$ to	Normal $C_3H_7\cdot OH$.	Normal $C_3H_7\cdot OH$ to	Iso $C_4H_9\cdot OH$.	Iso $C_4H_9\cdot OH$ to	Iso $C_5H_{11}\cdot OH$.	$H\cdot COOH$ to	$HC_3\cdot COOH$.
50............	1	1·045	1	1·062	1	1·027	1	1·059	1	1·059
100............	..	1·042	..	1·060	..	1·028	..	1·058	..	1·049
150............	..	1·042	..	1·060	..	1·027	..	1·059	..	1·049
200............	..	1·037	..	1·059	..	1·026	..	1·060	..	1·048
250............	..	1·037	..	1·059	..	1·026	..	1·059	..	1·048
300............	..	1·036	..	1·059	..	1·027	..	1·059	..	1·048
350............	..	1·036	..	1·058	..	1·028	..	1·057	..	1·047
400............	..	1·035	..	1·058	..	1·028	..	1·059	..	1·046
450............	..	1·035	..	1·056	..	1·028	..	1·059	..	1·044
500............	..	1·036	..	1·056	..	1·028	..	1·059	..	1·044
550............	..	1·036	..	1·054	..	1·028	..	1·059	..	1·014
600............	..	1·036	..	1·054	..	1·029	..	1·059	..	1·046
650............	..	1·035	..	1·053	..	1·029	..	1·059	..	1·047
700............	..	1·035	..	1·053	..	1·029	..	1·059	..	1·048
750............	..	1·036	..	1·051	..	1·029	..	1·059	..	1·049

Acids—*continued.*

Mm.	$CH_3 \cdot COOH$ to $C_2H_5 \cdot COOH$.		$C_2H_5 \cdot COOH$ to Iso $C_3H_7 \cdot COOH$.		Iso $C_3H_7 \cdot COOH$ to Iso $C_4H_9 \cdot COOH$.	
50....	1	1·071	1	1·037	1	1·053
100....	..	1·072	..	1·035	..	1·054
150....	..	1·069	..	1·031	..	1·056
200....	..	1·069	..	1·030	..	1·056
250....	..	1·067	..	1·031	..	1·053
300....	..	1·062	..	1·033	..	1·053
350....	..	1·061	..	1·033	..	1·052
400....	..	1·068	..	1·033	..	1·054
450....	..	1·061	..	1·032	..	1·051
500....	..	1·060	..	1·031	..	1·051
550....	..	1·059	..	1·031	..	1·051
600....	..	1·059	..	1·031	..	1·051
650....	..	1·057	..	1·032	..	1·051
700....	..	1·056	..	1·032	..	1·052
750....	..	1·054	..	1·031	..	1·053

Additional proof of the truth of the second relation is afforded by comparing the vapour-pressures of these compounds with those of water, that substance being taken as the standard, since the determinations of the vapour-pressures of water between 0° and 100° (*i.e.*, up to one atmosphere) are more trustworthy than those of any other substance. In the following table, in which the ratios of the absolute temperatures of the alcohols and acids to those of water are given, it is seen that the coefficient (C) of increase or decrease of the ratio per unit rise of temperature of the standard substance (water) is a constant.

The true values of C having been obtained graphically, the ratios found were corrected and the absolute temperatures of the acids and alcohols at the required pressures were calculated by multiplying those of water by the corrected ratios, the absolute temperatures were then reduced to degrees Centigrade and compared with the observed results.

It will be seen by referring to the annexed tables, that, with one or two exceptions, the two sets of numbers agree well. Obviously this is a simple method for smoothing the observed results of vapour-pressure determinations.

Ratio of the Absolute Temperatures of Alcohols and Acids to Water at Vapour-pressures between 50 mm. and 750 mm.

Alcohols.

Mm.	H_2O.	$CH_3 \cdot OH$.		$C_2H_5 \cdot OH$.		$C_3H_7 \cdot OH$.		$C_4H_9 \cdot OH$.		$C_5H_{11} \cdot OH$.	
		Observed.	Calculated. C=0·0007.	Observed.	Calculated. C=0·0009.	Observed.	Calculated. C=0·0025.	Observed.	Calculated. C=0·0022.	Observed.	Calculated. C=0·0025.
50....	1	0·9059	0·9066	0·9474	0·9474	1·0064	1·0064	1·0344	1·0314	1·0964	1·0950
100....	..	0·9079	0·9076	0·9455	0·9460	1·0021	1·0030	1·0311	1·0310	1·0918	1·0918
150....	..	0·9076	0·9080	0·9451	0·9454	1·0018	1·0010	1·0292	1·0291	1·0911	1·0898
200....	..	0·9096	0·9085	0·9435	0·9440	0·9997	0·9997	1·0262	1·0278	1·0890	1·0882
250....	..	0·9094	0·9090	0·9439	0·9444	1·0000	0·9984	1·0264	1·0267	1·0874	1·0870
300....	..	0·9090	0·9091	0·9429	0·9440	0·9983	0·9972	1·0261	1·0255	1·0860	1·0859
350....	..	0·9095	0·9095	0·9430	0·9438	0·9977	0·9963	1·0261	1·0250	1·0849	1·0850
400....	..	0·9101	0·9099	0·9424	0·9434	0·9966	0·9955	1·0247	1·0240	1·0830	1·0841
450....	..	0·9101	0·9102	0·9431	0·9431	0·9953	0·9949	1·0237	1·0233	1·0837	1·0834
500....	..	0·9110	0·9103	0·9434	0·9430	0·9958	0·9941	1·0225	1·0225	1·0824	1·0827
550....	..	0·9100	0·9105	0·9427	0·9427	0·9926	0·9935	1·0225	1·0221	1·0818	1·0820
600....	..	0·9099	0·9107	0·9414	0·9425	0·9911	0·9930	1·0215	1·0217	1·0810	1·0815
650....	..	0·9097	0·9108	0·9418	0·9424	0·9911	0·9925	1·0206	1·0212	1·0805	1·0810
700....	..	0·9093	0·9109	0·9418	0·9421	0·9903	0·9920	1·0205	1·0209	1·0804	1·0809
750....	..	0·9100	0·9110	0·9425	0·9420	0·9909	0·9915	1·0204	1·0204	1·0810	1·0800

Acids.

Mm.	H_2O.	H·COOH. Observed.	H·COOH. Calculated. C=0·0047.	CH_3·COOH. Observed.	CH_3·COOH. Calculated. C=0·0040.	C_2H_5·COOH. Observed.	C_2H_5·COOH. Calculated. C=0·0001.	C_3H_7·COOH. Observed.	C_3H_7·COOH. Calculated. C=0·0002.	C_4H_9·COOH. Observed.	C_4H_9·COOH. Calculated. C=0·0013.
50	1	0·9766	0·9774	1·0314	1·0271	1·1083	1·1083	1·1494	1·1450	1·2111	1·2100
100	..	0·9852	0·9838	1·0333	1·0321	1·1078	1·1086	1·1463	1·1448	1·2082	1·2082
150	..	0·9880	0·9878	1·0366	1·0356	1·1090	1·1087	1·1432	1·1447	1·2083	1·2073
200	..	0·9897	0·9906	1·0380	1·0380	1·1087	1·1087	1·1411	1·1445	1·2054	1·2066
250	..	0·9930	0·9929	1·0401	1·0401	1·1089	1·1087	1·1434	1·1440	1·2051	1·2060
300	..	0·9945	0·9946	1·0434	1·0420	1·1072	1·1088	1·1433	1·1443	1·2049	1·2054
350	..	0·9970	0·9963	1·0440	1·0430	1·1081	1·1088	1·1441	1·1442	1·2030	1·2049
400	..	0·9994	0·9980	1·0447	1·0447	1·1082	1·1088	1·1446	1·1441	1·2039	1·2044
450	..	1·0017	0·9990	1·0457	1·0458	1·1098	1·1088	1·1452	1·1440	1·2039	1·2040
500	..	1·0022	1·0040	1·0462	1·0469	1·1098	1·1088	1·1447	1·1440	1·2037	1·2038
550	..	1·0015	1·0017	1·0470	1·0470	1·1096	1·1089	1·1444	1·1440	1·2637	1·2033
600	..	1·0027	1·0028	1·0483	1·0489	1·1089	1·1089	1·1435	1·1439	1·2032	1·2030
650	..	1·0027	1·0038	1·0491	1·0498	1·1082	1·1089	1·1438	1·1439	1·2026	1·2038
700	..	1·0033	1·0046	1·0507	1·0507	1·1079	1·1089	1·1433	1·1439	1·2032	1·2025
750	..	1·0043	1·0055	1·0526	1·0514	1·1091	1·1689	1·1439	1·1439	1·2050	1·2023

Observed and Corrected Vapour-pressures compared.

Pres. in mm.	Methyl alcohol.		Ethyl alcohol.		Propyl alcohol.		Isobutyl alcohol.		Isoamyl alcohol.	
	Observed.	Calculated.	Observed.	Calculated.	Observed.	Calculated.	Observed.	Calculated.	Observed.	Calculated.
50	9·0	9·34	21·8	21·76	40·3	40·29	49·0	49·04	68·3	67·93
100	21·8	21·76	34·0	34·17	52·4	52·67	61·8	61·76	81·5	81·57
150	29·0	29·58	41·8	41·81	60·7	60·50	69·8	69·79	90·2	90·07
200	35·9	35·60	47·4	47·83	66·5	66·5	75·5	76·07	96·8	96·64
250	40·5	40·8	52·1	52·14	71·4	70·88	80·5	80·65	101·5	101·46
300	44·4	44·29	56·0	56·36	75·3	75·06	85·0	84·85	105·9	105·98
350	47·9	47·70	59·5	59·71	78·8	78·44	88·8	88·38	109·5	109·68
400	51·0	50·93	62·5	62·81	81·8	81·51	91·8	91·55	112·8	112·8
450	54·0	53·90	65·5	65·47	84·2	84·14	94·4	94·26	115·9	116·0
500	56·5	56·17	68·3	68·04	86·9	86·70	97·0	96·90	118·5	118·71
550	58·5	58·50	70·5	70·33	89·0	88·97	99·4	99·17	121·0	121·16
600	60·5	60·66	72·5	72·35	90·8	91·00	101·4	101·36	123·2	123·54
650	62·4	62·42	74·1	74·43	92·5	93·00	103·3	103·44	125·4	125·60
700	64·1	64·63	76·1	76·23	94·1	94·77	105·3	105·3	127·7	127·61
750	65·9	66·21	78·0	77·8	96·0	96·45	107·0	106·96	129·6	129·30

Observed and Corrected Vapour-pressures compared—continued.

Pres. in Mm.	Formic acid.		Acetic acid.		Propionic acid.		Isobutyric acid.		Isovaleric acid.	
	Observed.	Calculated.	Observed.	Calculated.	Observed.	Calculated.	Observed.	Calculated.	Observed.	Calculated.
50	31	31·44	48·1	46·70	72·0	72·0	84·8	83·43	104·0	104·91
100	46·9	46·40	62·5	62·20	86·7	86·86	99·2	98·71	119·3	119·53
150	56·1	56·10	72·3	71·90	96·4	96·4	107·8	108·30	129·5	129·28
200	63·1	63·37	79·5	79·53	103·5	103·44	114·5	115·6	136·5	136·89
250	69·0	68·92	85·5	85·17	108·9	108·76	120·8	121·10	142·0	142·41
300	74·1	73·98	90·7	90·45	113·3	113·79	125·9	126·21	147·4	147·66
350	78·8	78·33	95·1	94·83	117·7	117·89	130·4	130·43	151·5	151·92
400	82·8	82·30	98·9	98·91	121·5	121·70	134·5	134·49	155·5	155·87
450	86·5	85·61	102·2	102·40	125·3	124·95	138·0	137·58	159·0	159·18
500	89·5	88·75	105·4	105·70	128·4	128·06	141·0	140·77	162·2	162·28
550	92·0	91·77	108·3	108·68	131·1	130·85	143·8	143·63	165·0	165·30
600	94·5	94·41	111·2	111·38	133·4	133·39	146·1	146·27	167·8	167·8
650	96·7	96·97	113·8	113·95	135·6	135·83	148·7	148·77	170·4	170·54
700	98·9	99·41	116·5	116·50	137·7	138·07	150·8	151·08	173·0	172·95
750	101·0	101·45	119·0	119·43	140·0	139·96	153·0	153·0	175·8	174·78

LXXIV.—*On the Magnetic Rotation of Mixtures of Water with some of the Acids of the Fatty Series, with Alcohol, and with Sulphuric Acid; and Observations on Water of Crystallisation.*

By W. H. Perkin, Ph.D., F.R.S.

From my previous work on the magnetic rotation of compounds, it will be seen that the molecular rotation of water, which is taken as unity, is not the same as the sum of the values of oxygen and two of hydrogen, as deduced from the molecular rotation of other compounds. Thus, hydrogen is found to be 0·254, whilst oxygen in hydroxyl varies from 0·194 in ordinary alcohols to 0·137 in monobasic acids, and is 0·261 in carbonyl, so that, taking the lowest numbers, it gives $H_2 + O = 0{\cdot}645$, and taking the highest it is 0·769, instead of 1·0.

From these facts, it appeared that the determination of the magnetic rotation of hydrated compounds might give numbers which would indicate whether they still contained water, or whether the water and the substances with which it was mixed had combined so as to form new compounds. Thus, if the former were the case, the numbers should represent the value of the compound + the value of water; if the latter, the values should be lower than this. For example, if formic acid were mixed with water in the proportion of equal molecules of each, we may either get $HCOOH + H_2O$ or $HC(HO)_3$. The first would give—

Formic acid	1·671
Water.....................	1·000
	2·671

whilst the latter would give a number considerably lower than this; for instance, taking the highest values for $H_2 + O$ given above, it would be—

Formic acid	1·671
$H_2 + O$	0·769
	2·340

The same thing would be true of acetic acid and other members of the fatty series.

Since it has been believed that some of the fatty acids do unite with water to form trihydric alcohols, their examination appeared to be of special interest.

It is known that on adding water to formic acid, using molecular

proportions, a rise of temperature takes place, with an increase of density; the product also has a constant boiling point of 107° (Roscoe, *Chem. Soc. J.*, 1862, **15**, 271), giving it the appearance of a definite compound.

Acetic acid, on the other hand, when mixed with water—molecular proportions being used—gives rise to a very considerable reduction of temperature, but at the same time yields a product of greater density than acetic acid itself, which is very remarkable. The boiling point of this product is only approximately constant.

Propionic acid was found to behave in the same way as acetic acid, a very considerable reduction of temperature taking place on the addition of water, whilst the density was increased.

Butyric and isobutyric acids were also found to give a reduction of temperature when diluted with water, using about molecular proportions, but the densities were not taken, nor were they further examined.

Whilst examining these acids, it was thought advisable to determine the rotation of some hydrated substance which could not be a definite compound, for the sake of comparison, and for this purpose a mixture of absolute alcohol and water in molecular proportions was used. The following are the particulars respecting the products examined and their magnetic rotation:—

Hydrated Formic Acid.

The density of the formic acid used was $d\frac{15^\circ}{15^\circ}$ 1·22734. It was mixed with water in the proportion of one molecule of acid to one of water; this caused a considerable rise of temperature. The density of the product was—

$$d\frac{4^\circ}{4^\circ}\ 1{\cdot}1829,$$

$$d\frac{15^\circ}{15^\circ}\ 1{\cdot}16977,$$

$$d\frac{25^\circ}{25^\circ}\ 1{\cdot}16460.$$

If the water and formic acid had mixed without any change of volume the density would have been—

$$d\frac{15^\circ}{15^\circ}\ 1{\cdot}15358,$$

therefore condensation had taken place sufficient to cause a variation of 0·01619 in density.

The measurements of the magnetic rotation gave the following numbers :—

t.	Sp. rotation.	Mol. rotation.
19·8°	0·8767	2·671
19·8	0·8726	2·659
19·8	0·8752	2·667
19·8°	0·8748	2·666

Hydrated Acetic Acid.

The acetic acid used had a density of $d\frac{15^\circ}{15^\circ}$ 1·05704. It was diluted in the proportion of one molecule of acid to one molecule of water. Considerable reduction of temperature took place on making the mixture. The density of the product was—

$$d\frac{15^\circ}{15^\circ}\ 1{\cdot}07566,$$

$$d\frac{20^\circ}{20^\circ}\ 1{\cdot}07163,$$

$$d\frac{25^\circ}{25^\circ}\ 1{\cdot}06786.$$

The density of the above mixture if no change of volume had taken place would be—

$$d\frac{15^\circ}{15^\circ}\ 1{\cdot}04331.$$

Condensation had therefore occurred—although a large reduction of temperature had taken place when making the mixture—equal to a change of density of 0·03235, or twice as much as that in the case of formic acid.

The numbers obtained for the magnetic rotation were as follows :—

t.	Sp. rotation.	Mol. rotation.
16·0°	0·8818	3·555
16·0	0·8817	3·555
19·4	0·8800	3·558
19·4	0·8784	3·551
19·4	0·8784	3·551
18·0°	0·8801	3·554

Hydrated Propionic Acid.

The density of the acid used was $d\frac{15^\circ}{15^\circ}$ 0·99833. It was mixed in the proportion of equal molecules. *Considerable reduction of temperature* took place during the operation.

The density of the product was as follows:—

$$d\frac{4^\circ}{4^\circ}\ 1{\cdot}03448,$$

$$d\frac{15^\circ}{15^\circ}\ 1{\cdot}02494,$$

$$d\frac{25^\circ}{25^\circ}\ 1{\cdot}01729.$$

If no change of volume had occurred, it should have been $d\frac{15^\circ}{15^\circ}$ 0·99863. Therefore there was an increase of density equal to 0·02631.

The determination of the magnetic rotation gave the following numbers:—

t.	Sp. rotation.	Mol. rotation.
19·2°	0·9034	4·519
19·2	0·8964	4·485
19·2	0·8996	4·500
19·5	0·9030	4·519
19·6	0·9027	4·525
19·1	0·9013	4·516
19·1	0·9022	4·520
19·4°	0·9012	4·512

Hydrated Ethyl Alcohol.

The alcohol and water were mixed in molecular proportions, as in the other cases. As is well known, a result of this operation is a rise of temperature. The density of the product was—

$$d\frac{4^\circ}{4^\circ}\ 0{\cdot}87682,$$

$$d\frac{15^\circ}{15^\circ}\ 0{\cdot}86862,$$

$$d\frac{25^\circ}{25^\circ}\ 0{\cdot}86178.$$

If no change of volume had taken place the, density would have been $\frac{15^\circ}{15^\circ}$ 0·85837, showing that condensation had taken place to the extent of 0·01025 increase in density.

The following numbers were obtained for its magnetic rotation :—

t.	Sp. rotation.	Mol. rotation.
19·4°	0·9206	3·782
19·4	0·9226	3·790
19·4	0·9224	3·789
19·4°	0·9219	3·787

If now a comparison of these results be made with the calculated values of the products as composed of water and the acids or alcohols, we get the following :—

	Calculated.		Found.
CH_2O_2	1·671	2·671	2·666
H_2O	1·000		
$C_2H_4O_2$	2·525	3·525	3·554
H_2O	1·000		
$C_3H_6O_2$	3·462	4·462	4·512
H_2O	1·000		
C_2H_6O............	2·780	3·780	3·787
H_2O	1·000		

From these numbers it will be seen that these products behave as composed of the acids or alcohol and water, and not, as was considered to be the case, with the acids as trihydric alcohols, which would have given *lower* molecular rotations, in fact in the case of acetic and propionic acids, the numbers are inclined to be a little high. This, however, may be accidental.

The molecular rotation of glycerol, which has the same composition as propionic acid + one molecule of water, is 4·111. The distribution of the hydroxyl in this, however, is not the same as it would be in a compound derived from water and propionic acid, if formed.

The foregoing results are further evidence of the fact that although thermal changes and alterations of density result from chemical action, yet that they themselves are not evidence of chemical action. Bussy and Buignet have shown, for example, that when equal weights of chloroform and ethyl oxide are mixed, that a rise of temperature of 14·4° takes place, whereas chloroform and alcohol only give a rise of 2·90°, and chloroform and carbon bisulphide give a reduction of 5° (*Compt. rend.*, **59**, 676). I have also lately tried experiments roughly

with the following mixtures, which all give a reduction of temperature, viz.:—

Heptane and alcohol.
Tetrachloride of carbon and alcohol.
" " and acetic acid.
Ethyl iodide and alcohol.
Carbon bisulphide and acetic acid.

Tetrachloride of carbon with ether gives a rise of temperature, but not nearly so much as chloroform. In these cases, we have no ground for supposing that any chemical change results from the mixing of the products.

After obtaining the foregoing results with the fatty acids and alcohol, it was thought that it would be interesting to examine sulphuric acid in its pure and hydrated condition, as it is generally supposed to form two or more well-defined compounds with water.

The first might be either $H_2SO_4 + H_2O$ or $(HO)_4SO$. The product of this composition solidifies at 8° or 9°, forming six-sided prisms, and is known as glacial sulphuric acid.

The second might be either $H_2SO_4 + 2H_2O$ or $(HO)_4SO + H_2O$, or $(HO)_6S$. Sulphuric acid mixed with this proportion of water gives a product with the maximum condensation which results from the union of this acid with water.

The third might be either $H_2SO_4 + 3H_2O$ or one of the preceding compounds *plus* water. It must contain water. These three have all been examined.

As most of my work on the magnetic rotation has been in reference to compounds containing carbon, it was thought advisable to examine not only sulphuric acid, but also one of its ethers, to see if the relationship of the acid to the ethers would be at all comparable with that existing between an acid containing carbon and its ether. This would serve as an indication as to whether sulphuric acid behaves in relation to its magnetic rotation in a way analogous to other substances which have hitherto been examined. Methyl sulphate was selected for this purpose.

Sulphuric Acid, H_2SO_4.

For the acid used, I am indebted to the kindness of Dr. Messel. It was made by the admixture of fuming acid to acid of the ordinary strength, the percentage being determined both by volumetric and gravimetric methods. The density determinations gave—

$$d\frac{15°}{15°}\ 1{\cdot}83904,$$

$$d\frac{20^\circ}{20^\circ}\ 1{\cdot}83562,$$

$$d\frac{25^\circ}{25^\circ}\ 1{\cdot}83265,$$

At $\frac{15^\circ}{4^\circ}$ this will be 1·83748. Lunge (*Jour. Soc. Chem. Ind.*, **2**, 1883, 279) found for acid of this quality $\frac{15^\circ}{4^\circ}$ 1·8384.

The determinations of the magnetic rotation gave—

t.	Sp. rotation.	Mol. rotation.
19·5°	0·7809	2·316
20·0	0·7809	2·316
20·5	0·7810	2·317
21·0	0·7787	2·310
20·25°	0·7804	2·315

Hydrated Sulphuric Acid, $H_2SO_4 + H_2O$.

The density determinations of this product gave the following numbers:—

$$d\frac{15^\circ}{15^\circ}\ 1{\cdot}77806,$$

$$d\frac{20^\circ}{20^\circ}\ 1{\cdot}77423,$$

$$d\frac{25^\circ}{25^\circ}\ 1{\cdot}77071.$$

This at $\frac{15^\circ}{4^\circ}$ is 1·77655, and contains 84·4 per cent. H_2SO_4. The density of acid containing 84 per cent. H_2SO_4 is given as 1·7770.

The following numbers were obtained for its magnetic rotation:—

t.	Sp. rotation.	Mol. rotation.
20·0°	0·8799	3·196
20·0	0·8764	3·184
20·0	0·8773	3·187
20·4	0·8769	3·186
20·4	0·8770	3·186
20·16°	0·8775	3·188

Hydrated Sulphuric Acid, $H_2SO_4 + 2H_2O$.

The density determinations of this were as follows:—

$$d\frac{15^\circ}{15^\circ}\ 1{\cdot}65084,$$

$$d\frac{20^\circ}{20^\circ}\ 1{\cdot}64754,$$

$$d\frac{25^\circ}{25^\circ}\ 1{\cdot}64467.$$

The numbers obtained for its magnetic rotation were—

t.	Sp. rotation.	Mol. rotation.
20·5°	0·9101	4·113
20·5	0·9099	4·112
21·0	0·9109	4·117
21·0	0·9091	4·109
20·75°	0·9100	4·113

Hydrated Sulphuric Acid, $H_2SO_4 + 3H_2O$.

The density of this substance was found to be—

$$d\frac{15^\circ}{15^\circ}\ 1{\cdot}55064,$$

$$d\frac{20^\circ}{20^\circ}\ 1{\cdot}54754,$$

$$d\frac{25^\circ}{25^\circ}\ 1{\cdot}54493.$$

The magnetic rotation determinations gave—

t.	Sp. rotation.	Mol. rotation.
23°	0·9270	5·064
23	0·9245	5·050
23	0·9291	5·075
23	0·9281	5·069
23°	0·9272	5·064

Methyl Sulphate.

This ether was prepared by treating methyl alcohol with four or five times its weight of 60 per cent. fuming sulphuric acid, distilling the mixture, washing the ether first with water and then with dilute

carbonate of sodium solution, quickly drying over potassium carbonate, and distilling several times. As thus obtained, it boiled between 188·3—188·6° (corr.). The density determinations gave—

$$d\frac{15^\circ}{15^\circ}\ 1{\cdot}33344,$$

$$d\frac{20^\circ}{20^\circ}\ 1{\cdot}32757,$$

$$d\frac{25^\circ}{25^\circ}\ 1{\cdot}32386.$$

The magnetic rotations obtained were as follows:—

t.	Sp. rotation.	Mol. rotation.
22·8°	0·7590	4·007
22·8	0·7605	4·015
22·8	0·7611	4·018
22·8°	0·7602	4·013

It will be best perhaps first to consider the rotation of sulphuric acid in relation to methyl sulphate.

If we subtract the rotation of the acid from the ether, we get the following result:—

Methyl sulphate	4·0130
Sulphuric acid...........	2·3150
	1·6980

This is the influence of replacing two of hydrogen by two of methyl, or 0·849 for one of methyl.

Now if we take some of the fatty acids and their ethers, and subtract them, we get—

Methyl formate............	2·495
Formic acid	1·671
	0·824
Methyl acetate	3·362
Acetic acid................	2·525
	0·837
Methyl butyrate	5·387
Butyric acid	4·472
	0·915

It will be seen that the number obtained from sulphate of methyl agrees closely with that of methyl formate and methyl acetate, but not so well with methyl butyrate, which is the second member of the true homologous series in which this last number for methyl is constant. It is, however, I think, quite natural that owing to its highly chlorous nature, it should be most nearly comparable with formic or acetic compounds, and there is, therefore, no reason to doubt that sulphuric acid and its compounds, in regard to their magnetic rotation, behave in a manner analogous to other compounds.

With respect to the rotations of the hydrated sulphuric acids, the results are not so clear as in the case of the hydrated fatty acids, as the following comparisons will show:—

	Calculated.		Found.
Sulphuric acid	2·315	3·315	3·188
H_2O	1·000		
Sulphuric acid	2·315	4·315	4·113
$2H_2O$	2·000		
Sulphuric acid	2·315	5·315	5·064
$3H_2O$	3·000		

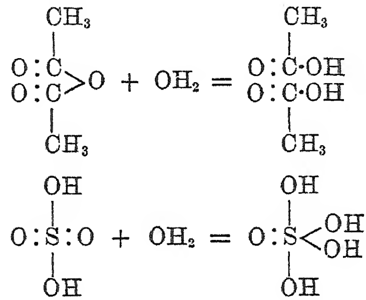
Here we get lower rotations indicating combination. In the first instance, we get an increase of rotation, owing to the water added, of 0·873, in the second of 0·925, and in the third of 0·951, instead of 1·0, which is the value of water, the last number being, however, very near to this. These numbers indicate that the largest amount of combination takes place when the first molecule is added, and but very little when the third is added, in fact it would appear that sulphuric acid with one molecule of water forms the compound $(HO)_4SO$, but that all the acid cannot exist as this without the presence of a larger amount of water. Now if we take the rotation of the product made by adding three molecules of water to sulphuric acid, and subtract the value of sulphuric acid from it, we get—

H_2SO_4 $3H_2O$	5·064
H_2SO_4	2·315
Influence of 3 mols. of water added .	2·749

This value is equal to that of two molecules of water + 0·749; therefore if the compound $(HO)_4SO$ has been formed its rotation will be that of sulphuric acid + this number. Is this likely to be the case?

I have lately been examining the rotation of the anhydrides of the

fatty acids, and the results obtained I think will go to answer this question, seeing that the rotation of the hydrated anhydrides or acids are also known. There is a close analogy between the formation of an acid by the action of water on an anhydride of a fatty acid and the formation of such a compound as $(HO)_4SO$ from sulphuric acid. Thus, taking acetic anhydride—



in both cases one atom of oxygen of the compound and one molecule of water go to form two hydroxyls; in the one case the product splits up into two molecules, in the other it remains a single one.

The molecular rotations of acetic and propionic anhydrides are given below, and subtracted from the molecular rotation of the two molecules of the respective acids which result from their combination with water. This will give a number representing the increase of rotation due to the combination of a molecule of water.

Rotation of acetic acid $= 2{\cdot}525 \times 2 =$	$5{\cdot}050$
,, acetic anhydride	$4{\cdot}282$
	$0{\cdot}768$
Rotation of propionic acid $= 3{\cdot}462 \times 2 =$	$6{\cdot}924$
,, propionic anhydride	$6{\cdot}185$
	$0{\cdot}739$

Now it will be seen that these numbers correspond very closely with the residual number obtained above in the case of sulphuric acid, viz., 0·749, so that the probability of the compound $(HO)_4SO$ being the result of the addition of water to sulphuric acid becomes very strong, especially as the rotations cannot in any way be made to agree with the formation of $(HO)_6S$, the numbers being too high; in fact only one chemical compound seems to result from the action of water on sulphuric acid, namely, $(HO)_4SO$.

Experiments are in progress on the other sulphuric compounds, and it is also proposed to examine sulphurous compounds.

Whilst working on hydrated products, my attention has been drawn to the subject of water of crystallisation. The point which has struck me most is the want of consistency as to the presence or absence of water of crystallisation in the simple salts of metals belonging to the same class. Take, for example, the salts of silver, potassium, and sodium. The silver salts are mostly anhydrous, the larger number of potassium salts are also anhydrous, whilst sodium salts generally contain water of crystallisation. Moreover, when analogous salts of similar metals contain water of crystallisation, the proportions are not the same, as in K_2CO_3, and Na_2CO_3. These instances might be greatly multiplied. Amongst carbon compounds there is also a very remarkable instance of this inconsistency. I refer to the crystalline compound of methyl bromide and water (from my determinations, this consists of 1 mol. methyl bromide to about 10 mols. H_2O; Merritt gives it as probably containing 20 mols. H_2O, *J. pr. Chem.* [2], **18**, 293). This substance stands quite alone, no other related halogen carbon compound behaving in a similar manner.

These inconsistencies are in fact so great that it is impossible to believe that water of crystallisation has any relationship to chemical combination. Of course hydrogen and oxygen may be contained in some salts in the proportions found in water, and be chemically combined,* but then they are not in the form of water. For example, copper and magnesium sulphates do not lose what is supposed to be the last molecule of water which is contained in the crystallised salt unless very strongly heated. This hydrogen and oxygen, however, may not be in the form of water, but the compounds may correspond to the substance which is obtained by mixing sulphuric acid with water, viz., $(HO)_4SO$, and be constituted thus—

$$\left.\begin{matrix} R''O_2 \\ (HO)_2 \end{matrix}\right\} SO.$$

What, then, can be the relationship of water of crystallisation to chemical compounds? It appears to me that it is in all probability purely *physical*, its presence with the compound being necessary for the building up of the crystalline form which can most readily be produced.

We know that the crystalline form of a substance containing water of crystallisation is essentially connected with the amount of water it contains. For example, sodium carbonate may be taken, which crystallises with one, five, six, eight, and ten molecules of water, varying

* By chemical combination, I mean that which takes place between molecules of different kinds, whereby they are more or less broken up, and the constituents rearranged so as to form new molecules; or that which takes place when different molecules act on each other so as to produce new molecules not containing either of the original ones used in their production.

in form (that with 10 mols. being the most easily produced, though, if chemical combination had to do with its formation, we should have expected it to be the most difficult, as it should be the least stable).

Again in products where the proportion of water is constant, the crystalline form often remains practically unchanged although the other constituents may be varied. Take, for example, the large number of alums which contain 24 molecules, or nearly half their weight of water; also the large number of substances isomorphous with ammonium magnesium sulphate containing 6 mols. H_2O, and the sulphates of magnesium, nickel, and zinc. The sodium salts, with 10 mols. H_2O, such as the carbonate, sulphate, chromate, and pyrophosphate, are also all said to belong to the oblique prismatic system, showing the important part water must play in reference to form.

The amount of water of crystallisation in some of the above-mentioned substances, if taken in reference to the amount of water in the salts from which they are formed, is also worth considering. Take potassium and sodium alums. The former is made from potassium sulphate, which is anhydrous, and aluminium sulphate, which contains 18 mols. H_2O; the alum contains 6 mols. *more* H_2O. The latter is made from sodium sulphate, which usually contains 10 mols. H_2O, and sulphate of alumina, which contains 18, making 28 in all; the alum contains 4 mols. *less*. Again, take iron alum. The potassium sulphate is anhydrous; the ferric sulphate contains 9 mols. H_2O. This is 15 mols. *less* than is contained in the resulting alum. With the compounds of the ammonium magnesium sulphate class we find much the same thing. Magnesium sulphate contains 7 mols. H_2O; the so-called double salt contains 6, or one less. When copper sulphate, which usually contains only 5 mols. H_2O, is used in place of magnesium sulphate, the so-called double salt also contains 6 mols., or in this case one more than the copper sulphate used.

From these changes in the amount of water of crystallisation, it seems that we cannot assume that its relation to a salt or other compound has any connection with chemical combination, otherwise the influence of the water contained in the substances used in the preparation of these compounds would be in some way exhibited in the product formed. For example, sodium salts nearly always contain a large amount of water of crystallisation. If this were due to chemical union, this should certainly manifest itself in sodium alum, but it does not. We find, however, in the isomorphous compounds referred to, that the crystalline form and the proportion of water of crystallisation remain the same in each group, and if, therefore, the water is not chemically combined, its association with the chemical compound would appear to be in relation to the building up of the crystalline form. It is difficult to see what other part it can play.

Why, then, do some compounds crystallise without, and some with water of crystallisation? The answer to this is, probably, that if a salt by itself can produce the most easily formed crystalline structure, that it will naturally do so, and be anhydrous, but if, on the other hand, it cannot do so, that it will associate itself with that number of molecules of water with which it can most readily produce the crystalline form.

These observations would equally apply to compounds crystallising with alcohol, acetic acid, benzene, &c., and to some double salts, one or more of the constituents acting like water of crystallisation.

There is one point of interest which should result if the above view respecting water of crystallisation be correct, and that is in reference to the subject of solution. It is evident that if water of crystallisation be only related to crystalline form, this water will no longer be attached to the compound with which it is associated on the breaking up of this form by solution. And this is believed to be the case by many who have studied the subject of solution.

I have ventured to bring these observations forward, although in a rather incomplete way, thinking that the subject of water of crystallisation is well worth considering from this point of view.

LXXV.—*Evaporation and Dissociation.* Part IV. *A Study of the Thermal Properties of Acetic Acid.*

By WILLIAM RAMSAY, Ph.D., and SYDNEY YOUNG, D.Sc.

1. The abnormal behaviour of acetic acid and homologous acids has rendered them the subject of numerous investigations. At moderately low temperatures, these substances invariably show vapour-densities, which would lead to the conclusion that the structure of their molecules is not so simple as that expressed by their formulæ. But although many experiments have been made, especially with acetic acid, no complete research is on record, showing the influence of pressure and temperature on the density of its vapour, and on the heats of volatilisation. It is only necessary to name Playfair and Wanklyn, Cahours, Bineau, Horstmann, and Naumann, to indicate the importance attached to this subject. The results of these experimenters shall be considered later.

2. *Material used in this Research.*—The sample of acid used was a portion of the stock with which we have already experimented. To quote from a previous paper on the vapour-pressures of acetic acid

(*Trans. Roy. Soc.*, 1884, ii, 469), "The acid which we used for these experiments was a portion of a stock of glacial acid obtained for laboratory purposes several years ago. The liquid portions had been poured off from time to time, as required for laboratory use. A very complete series of fractionations has thus unwittingly been carried out, and it is now so pure that at a temperature slightly below its melting point, it is completely solid." After an aqueous portion of about 400 c.c. had distilled off, the boiling point became practically constant, and remained constant until the last trace of the remaining 200 c.c. had distilled over. The rise in temperature did not amount to 0·05° during the distillation of the last portion. It will be afterwards shown that the density of this sample is nearly the same as that found by Perkin, who took especial pains to purify and dry his acid; but we are of opinion that any attempt to dry the acid by the ordinary desiccatory reagents introduces acetic anhydride. It is doubtful whether the want of constancy in the boiling point of Perkin's sample of acid was due to this cause, or to the presence of homologous acids; but it may here be noticed that we ourselves attempted to obtain a product of constant boiling point from a specimen of ordinary glacial acid, freshly purchased, and were unable to do so. As a test of purity, we may mention that identical vapour-pressures were obtained with several samples of acid fractionated from the stock above referred to, by both the dynamical and statical methods, and this is, according to Regnault, a crucial test of purity. He says:—"Lorsqu'une liquide renferme une portion même extrêmement petite d'une autre substance volatile, les deux méthodes donnent des valeurs différentes pour les forces élastiques de sa vapeur à la même température; et c'est un moyen extrêmement délicat pour juger de l'homogénéité d'une substance volatile." (*Mémoires de l'Academie*, **26**, 341.)

3. *Apparatus Employed.*—As a full description of the apparatus used has been given in a paper on the thermal constants of ether, recently communicated to the Royal Society, it is unnecessary to describe them further here, than merely to state that the vapour-densities at low temperatures were determined by a modification of Hofmann's apparatus, in which pressure, temperature, and volume could be altered at will; and at high temperatures by a modified Andrews' apparatus, provided with two air-gauges, one for registering high and the other low pressures. The calibration of the gauges and of the volume-tube has, moreover, been fully described, and also the method of reducing the results. The temperatures were controlled by the method which we have already described in the *Transactions of the Chemical Society*, 1885, 640. The results recently obtained by Amagat for the compressibility of air were introduced in calculating pressures (*Compt. rend.*, **99**, 1153).

Experimental Results.

4. *Vapour-pressures at Low Temperatures.*—These constants were determined by us in 1884. A full account of the method of research and a statement of the results is to be found in the *Phil. Trans.*, 1884, 465, and in this Journal (Trans., 1885, 42).

5. *Vapour-densities in Hofmann's Apparatus.*—The acetic acid taken was weighed out in a small tube, and introduced into the Hofmann's apparatus. We append an example of the method of calculation, which will give an idea of the corrections introduced.

Barometric pressure..................	759·8 mm.
Height of mercury in gauge...........	536·75 ,,
Modified atmospheric pressure	223·05 ,,
Height of mercury in Hofmann's tube ..	209·9 ,,
Height of mercury in bottle	0·0 ,,
Difference	209·9 ,,
Correction for temperature of mercury in tube..........................	0·45 ,,
Vapour-pressure of mercury	0·1 ,,
Corrected height of mercury column at temperature of room................	209·55 ,,
Correction for capillarity of differential gauge	0·1 ,,
Uncorrected pressure of vapour, 222·95—209·55 = ...	13·4 ,,
Corrected to 0°	13·35 ,,
Volume of gas at temperature 50°......	170·06 c.c.
Weight	0·01126 gram.
Vapour-density.....................	49·58.

6. Weight taken, 0·01126 gram.

Pressure of Alcohol Vapour 220 mm.; Temp. 50°.

Pressure.	Volume.	Vapour-density.	Pressure.	Volume.	Vapour-density.
13·4 mm.	170·06 c.c.	49·58	26·5 mm.	79·96 c.c.	53·27
15·4 ,,	150·10 ,,	48·88	30·0 ,,	69·97 ,,	53·83
16·95 ,,	134·88 ,,	49·43	34·9 ,,	60·00 ,,	53·84
18·2 ,,	119·80 ,,	51·83	51·35 ,,	40·17 ,,	54·79
21·0 ,,	105·00 ,,	51·25	56·0 ,,	33·2 ,,	60·78 (liquid present)
24·15 ,,	90·08 ,,	51·94	57·2 ,,	25·3 ,,	78·08 (liquid present)

7. Pressure of Alcohol Vapour 761 mm.; Temp. 78·4°.

Series I.

Pressure.	Volume.	Vapour-density.	Pressure.	Volume.	Vapour-density.
18·80 mm.	163·8 c.c.	39·91	125·3 mm.	19·9 c.c.	49·17
20·95 "	149·98 "	39·14	141·3 "	17·1 "	50·87
23·35 "	135·1 "	38·97	164·2 "	14·7 "	50·93
27·3 "	111·0 "	40·56	187·1 "	12·25 "	53·64
32·7 "	88·2 "	42·61			(liquid ?)
42·05 "	68·4 "	42·74	194·2 "	9·2 "	68·81
52·90 "	52·15 "	44·57			(liquid)
71·7 "	36·95 "	46·40	197·3 "	7·7 "	80·92
91·2 "	28·1 "	47·97			(liquid)

Series II.

Pressure.	Volume.	Vapour-density.	Pressure.	Volume.	Vapour-density.
19·3 mm.	166·2 c.c.	38·33	46·4 mm.	59·97 c.c.	44·15
21·1 "	149·2 "	39·05	54·35 "	50·01 "	45·24
22·85 "	134·9 "	39·88	66·75 "	40·01 "	46·04
21·85 "	140·01 "	40·19	87·2 "	30·06 "	46·90
23·45 "	130·01 "	40·33	101·25 "	25·0 "	48·56
24·90 "	120·06 "	41·14	124·65 "	20·06 "	49·16
27·00 "	110·06 "	41·39	151·7 "	16·0 "	50·64
27·15 "	109·9 "	41·20	172·25 "	14·0 "	50·98
29·3 "	99·85 "	42·02	199·65 "	8·0 "	76·96
31·8 "	90·06 "	42·92			(liquid)
35·85 "	79·86 "	42·94	194·75 "	11·0 "	57·38
40·15 "	70·0 "	43·74	191·75 "	12·0 "	53·43

8. Weight = 0·03565.

Temperature the same.

Pressure.	Volume.	Vapour-density.	Pressure.	Volume.	Vapour-density.
63·2 mm.	137·8 c.c.	44·65	188·55 mm.	38·95 c.c.	52·94
106·6 "	76·0 "	47·99			(liquid)
121·5 "	65·1 "	49·16	190·55 "	36·45 "	55·99
157·75 "	49·0 "	50·31			(liquid)
180·8 "	41·88 "	51·36	192·05 "	28·77 "	70·38
					(liquid)

9. Weight = 0·01126.

Jacketed with Acetic Acid; Pressure 314 mm.; Temp. 92·0°.

Pressure.	Volume.	Vapour-density.	Pressure.	Volume.	Vapour density.
20·45 mm.	165·0 c.c.	37·85	96·80 mm.	29·83 c.c.	44·22
24·55 „	135·0 „	38·53	138·6 „	20·18 „	45·66
30·58 „	105·0 „	39·80	181·05 „	14·94 „	47·21
39·35 „	80·0 „	40·57	308·6 „	5·88 „	70·35 (liquid)
51·10 „	60·0 „	41·64			
66·45 „	45·04 „	42·66			

10. Weight = 0·03565.

Temperature the same.

Pressure.	Volume.	Vapour-density.	Pressure.	Volume.	Vapour-density.
75·65 mm.	125·3 c.c.	42·66	303·5 mm.	24·0 c.c.	55·51 (liquid)
104·2 „	87·0 „	44·70	300·4 „	25·41 „	52·97 (liquid)
135·8 „	65·05 „	45·78	296·95 „	26·29 „	51·79 (liquid)
170·8 „	50·0 „	47·35	292·9 „	27·0 „	51·13 (liquid ?)
234·9 „	35·0 „	49·18			
268·4 „	30·05 „	50·13			

11. Weight = 0·01126.

Pressure of Acetic Acid Vapour 498 mm.; Temp. 105·1°.

Pressure.	Volume.	Vapour-density.	Pressure.	Volume.	Vapour-density.
21·85 mm.	170·58 c.c.	35·49	155·4 mm.	20·02 c.c.	42·52
31·9 „	115·0 „	36·06	199·75 „	15·02 „	44·09
53·6 „	65·1 „	37·9	286·5 „	9·96 „	46·35
74·65 „	45·1 „	39·28	487·8 „	3·85 „	70·31 (liquid)
94·1 „	35·02 „	40·14			
126·3 „	25·0 „	41·89			

12. Weight = 0·03565.

Temperature the same.

Pressure.	Volume.	Vapour-density.	Pressure.	Volume.	Vapour-density.
83·45 mm.	128·0 c.c.	39·22	422·4 mm.	20·0 c.c.	47·75
106·3 ,,	97·0 ,,	40·63	460·35 ,,	18·0 ,,	49·58
150·4 ,,	65·0 ,,	42·85	480·5 ,,	16·0 ,,	50·55
186·2 ,,	51·0 ,,	44·11			54·47
232·6 ,,	40·0 ,,	45·02	474·5 ,,	17·15 ,,	(liquid)
298·6 ,,	30·0 ,,	46·76			51·46
337·4 ,,	26·0 ,,				(liquid)

13. Weight = 0·01126.

Pressure of Acetic Acid 751·8 mm.; Temp. 118·2°.

Pressure.	Volume.	Vapour-density.	Pressure.	Volume.	Vapour-density.
24·1 mm.	170·0 c.c.	33·39	88·6 mm.	42·58 cc.	36·27
29·1 ,,	140·0 ,,	33·58	121·5 ,,	30·0 ,,	37·53
36·65 ,,	110·0 ,,	33·93	172·6 ,,	20·05 ,,	39·55
44·0 ,,	89·9 ,,	34·59	224·2 ,,	15·03 ,,	40·62
55·3 ,,	70·0 ,,	35·35	319·0 ,,	9·87 ,,	43·48
69·25 ,,	55·0 ,,	35·93	391·9 ,,	7·76 ,,	45·02
84·05 ,,	45·15 ,,	36·06	433·6 ,,	6·88 ,,	45·89

14. Weight = 0·03565 gram.

Pressure of Acetic Acid 745·8 mm.; Temp. 117·95°.

Pressure.	Volume.	Vapour-density.	Pressure.	Volume.	Vapour-density.
75·75 mm.	160·0 c.c.	35·73	676·8 mm.	13·0 c.c.	49·26
85·35 ,,	138·0 ,,	36·77	722·4 ,,	10·1 ,,	59·42
163·5 ,,	66·6 ,,	39·78			(liquid)
210·45 ,,	50·0 ,,	41·17	712·8 ,,	11·05 ,,	55·04
256·4 ,,	39·95 ,,	42·30			(liquid)
328·6 ,,	30·0 ,,	43·96	706·5 ,,	12·0 ,,	51·13
386·1 ,,	25·0 ,,	44·89			(liquid)
467·1 ,,	20·0 ,,	46·39	733·5 ,,	8·0 ,,	73·93
601·8 ,,	15·0 ,,	48·01			(liquid)
632·5 ,,	14·0 ,,	48·95			

15. Pressure of Aniline 160 mm.; Temp. 132·9°.

Pressure.	Volume.	Vapour-density.	Pressure.	Volume.	Vapour-density.
101·7 mm.	128·0 c.c.	34·54	360·4 mm.	30·35 c.c.	41·11
132·7 „	95·0 „	35·67	470·7 „	22·0 „	43·42
174·5 „	70·2 „	36·71	700·2 „	13·95 „	46·03
214·9 „	55·1 „	37·98	747·6 „	13·0 „	46·27
285·2 „	40·0 „	39·43			

16. Pressure of Aniline 262·5 mm.; Temp. 147·6°.

Pressure.	Volume.	Vapour-density.	Pressure.	Volume.	Vapour-density.
88·5 mm.	161·0 c.c.	32·7	341·8 mm.	36·0 c.c.	37·87
133·9 „	100·0 „	34·8	427·9 „	28·0 „	38·88
181·6 „	72·9 „	35·19	507·0 „	23·0 „	39·95
225·1 „	58·0 „	35·69	602·5 „	19·0 „	40·70
263·5 „	48·2 „	36·68	729·7 „	15·0 „	42·57

17. Pressure of Aniline 416 mm.; Temp. 162·5°.

Pressure.	Volume.	Vapour-density.	Pressure.	Volume.	Vapour-density.
95·9 mm.	159·0 c.c.	31·64	450·5 mm.	30·0 c.c.	35·71
134·3 „	112·0 „	32·07	526·7 „	25·0 „	36·65
183·8 „	80·0 „	32·81	640·3 „	20·0 „	37·68
274·0 „	52·0 „	33·87	729·5 „	17·0 „	38·91
373·1 „	37·0 „	34·95			

18. Pressure of Aniline 754·7 mm.; Temp. 184·1°.

Pressure.	Volume.	Vapour-density.	Pressure.	Volume.	Vapour-density.
98·05 mm.	165·9 c.c.	31·13	425·7 mm.	36·0 c.c.	33·05
140·7 „	114·9 „	31·33	520·4 „	29·0 „	33·56
188·2 „	85·0 „	31·66	666·4 „	22·0 „	34·54
242·9 „	65·0 „	32·07	791·6 „	18·0 „	35·54
336·8 „	46·0 „	32·69			

Constants with Modified Andrews' Apparatus.

19. For these experiments, four different quantities of acetic acid were used. With the first and second, the expansion was determined;

with the third, the vapour-pressures and the vapour-densities near saturation point at the highest temperatures; and with the fourth, the densities of the saturated and unsaturated vapour.

20. *Weights of Substance Employed.*—The weights of the first three portions were determined by reading the volume at a known temperature and low pressure, and by determining the sp. gr. of the acid at a closely approximate temperature. The details are as follows:—

The determination was made in a Sprengel's tube of the form recommended by Perkin (Trans., 1884, 443).

Weight of acetic acid at 13·11°	39·5025 grams.
Weight of water at 13·20°	37·3558 ,,
Specific gravity at 13·11° (water at 4° = 1·0)	1·05682
Volume of 1 gram	0·94622 c.c.

(These weighings were reduced to a vacuum.)

Portion I.—Volume at 17·95°	0·65829 c.c.
Volume at 13·11°, graphically obtained from expansion	0·65593 ,,
Therefore weight	0·69322 gram.

The limit of accuracy in reading was here 1 in 2000.

Portion II.—Volume at 19·77°	0·20456 c.c.
Volume at 16·10°	0·20435 ,,
Volume at 13·11°, graphically obtained	0·20349 ,,
The weight is therefore	0·21505 gram.

The limit of accuracy in reading was here 1 in 500.

Portion III.—Volume at 14·5°	0·06987 c.c.
Specific gravity at 14·5°, calculated	1·0553
Hence weight	0·07374 gram.

Limit of accuracy 1 in 200.

This weight was used in calculating the vapour-density, but as a check on its correctness, a measurement at 279·85° was made.

Volume at 279·85°	0·11223 c.c.
Specific gravity	0·6595
Weight	0·07401 gram.

This, it will be seen, is within the limits of error.

Portion IV.—The weight of the fourth portion was determined by comparisons of the volumes of its unsaturated vapour with those of the third portion at the same pressures. The comparison was made graphically, and from it the weight was found to be equal to 0·005358 gram.

Expansion of Liquid.

21. First Portion. Weight = 0·69322 gram.

Jacketing vapours.	Pressure reduced to 0°.	Temperature on air thermometer.	Vol. of liquid.	Vol. of 1 gram.		Sp. gr.
				Read.	Smoothed.	
	mm.		c.c.			
	—	0°	—	—	0·9348	1·0697
	—	10	—	—	0·9440	1·0593
	—	17·95	0·65829	0·94962	0·9512	1·0513
	—	20·0	—	—	0·9532	1·0491
	—	30·0	—	—	0·9623	1·0392
Alcohol..........	133·7	40·0	0·67353	0·97160	0·9724	1·0284
"	220·0	50·0	0·68099	0·98236	0·9828	1·0175
"	350·3	60·0	0·68916	0·99415	0·9940	1·0060
"	541·2	70·0	0·69732	1·0059	1·0052	0·9948
Chlorobenzene	144·8	80·0	0·70528	1·0174	1·0168	0·9835
"	208·35	90·0	0·71307	1·0286	1·0290	0·9718
"	292·75	100·0	0·72230	1·0420	1·0418	0·9599
"	402·55	110·0	0·73151	1·0552	1·0545	0·9483
"	542·8	120·0	0·74093	1·0688	1·0682	0·9362
"	718·95	130·0	0·75105	1·0834	1·0828	0·9235

Second Portion. Weight = 0·21505 gram.

Jacketing vapours.	Pressure reduced to 0°.	Temperature on air thermometer.	Vol. of liquid.	Vol. of 1 gram.		Sp. gr.
				Read.	Smoothed.	
	mm.		c.c.			
Chlorobenzene	542·8	120°	0·22991	1·0691	1·0682	0·9362
"	718·95	130	0·23215	1·0795	1·0828	0·9235
Bromobenzene	372·65	130	0·23310	1·0839	1·0828	0·9235
"	495·80	140	0·23598	1·0973	1·0980	0·9108
"	649·05	150	0·23954	1·1139	1·1138	0·8978
Aniline..........	283·7	150	0·23954	1·1139	1·1138	0·8978
"	386·0	160	0·24343	1·1320	1·1301	0·8849
"	515·6	170	0·24666	1·1470	1·1481	0·8710
"	677·15	180	0·25090	1·1667	1·1678	0·8563
Methyl salicylate..	249·35	180	0·25090	1·1667	1·1678	0·8412
" " ..	330·85	190	0·25612	1·1910	1·1888	0·8412
" " ..	432·35	200	0·26082	1·2128	1·2117	0·8253
" " ..	557·5	210	0·26597	1·2368	1·2360	0·8091
" " ..	710·1	220	0·27147	1·2623	1·2632	0·7916
Bromonaphthalene	235·95	230	0·27782	1·2919	1·2933	0·7732
"	303·35	240	0·28455	1·3232	1·3270	0·7536
"	386·35	250	0·29423	1·3682	1·3640	0·7331
"	487·35	260	0·30235	1·4060	1·4060	0·7112
"	608·75	270	0·31329	1·4569	1·4561	0·6868
"	751·4	279·9	0·32609	1·5164 (280°)	1·5172	0·6591

Vapour-pressures and Vapour-densities.

22. The vapour-pressures and vapour-densities were determined with portions 3 and 4.

Portion 4. Weight = 0·005358 gram.

Jacketing vapours.	Pressure reduced to 0°.	Temperature on air thermometer.	Vapour-pressure.	Mean.
	mm.			
Aniline	144·7	130°	1035 1040 1044	1040
„	204·6	140	1376 1387 1384 1376	1381
„	283·7	150	1821 1834 1830 1843 1909	1847
„	386·0	160	2375 2368 2343 2398	2371

Jacketing vapour.	Pressure reduced to 0°.	Temperature on air thermometer.	Volume.	Pressure.	P.V.	Vapour-density.
	mm.		c.c.	mm.		
Aniline	416·0	162·5°	1·1630	1413	1644	44·12
„	„	„	1·0572	1526	1613	44·94
„	„	„	0·98623	1616	1594	45·49
„	„	„	0·87854	1777	1561	46·44
„	„	„	0·80660	1907	1538	47·15
„	„	„	0·73540	2049	1507	48·12
„	„	„	0·69991	2128	1490	48·68
„	„	„	0·66434	2212	1470	49·34
„	„	„	0·62883	2291	1441	50·33
„	„	„	0·59317	2390	1418	51·16
„	„	„	0·55760	2456	1370	52·96
						trace of liquid
„	„	„	—	2496 2541 2546 2527	Mean 2527 mm.	
„	515·6	170	—	3006 3040 3049	„ 3032 „	
„	677·15	180	—	3795 3831 3848 3844	„ 3829 „	
„	746·9	183·75	1·1636	1628	1894	40·14
„	„	„	1·0577	1760	1862	40·85

At this stage, a small quantity of acetic acid made its appearance at the lower end of the tube, and passed up, necessarily increasing the weight. To ascertain the amount of this increase, the readings just given were repeated, and as the increase was only about 0·2 per cent., it was considered that at the same volumes the vapour-density would be uninfluenced. The weight was increased from 0·005358 to 0·005368 gram. This weight applies only to this series which was the last of our experiments.

Jacketing vapour.	Pressure reduced to 0°.	Tempera-ture on air ther-mometer.	Volume.	Pressure.	P.V.	Vapour-density.
	mm.			mm.		
Aniline	745·9	183·7°	1·1636	1630	1897	40·16
"	"	"	1·0577	1764	1866	40·83
"	"	"	0·98678	1876	1851	41·15
"	"	"	0·87902	2066	1817	41·94
"	"	"	0·77135	2299	1773	42·96
"	"	"	0·66471	2599	1728	44·09
"	"	"	0·55791	2993	1669	45·63
"	"	"	0·45183	3511	1587	48·03
"	"	"	0·41677	3733	1556	48·97
"	"	"	0·38181	3932	1502	50·76 (liquid)

Pressure of Aniline.

Pressure reduced to 0°.	Tempera-ture on air ther-mometer.	Pressure.
		mm.
745·9 mm.	183·7°	4149, 4135, 4155, 4167 — Mean 4152 mm.

Pressure of Methyl Salicylate.

Pressure reduced to 0°.	Temperature on air thermometer.	Volume.	Pressure.	P.V.	Vapour-density.
mm.		c.c.	mm.		
249·35	180°	—	3817	—	—
330·85	190	—	4751 4765	Mean 4758 mm.	
432·35	200	1·1633	1780	2072	38·02
,,	,,	1·0225	1984	2030	38·80
,,	,,	0·84318	2341	1974	39·91
,,	,,	0·66484	2852	1896	41·53
,,	,,	0·48711	3679	1792	43·96
,,	,,	0·38189	4452	1701	46·32
,,	,,	0·31215	5178	1616	48·73
,,	,,	0·27723	5607	1554	50·67 (liquid)
,,	,,	0·25975	5760	1500	52·49 (liquid)
,,	,,	—	5854 5866	Mean 5860 mm.	
557·5	210	—	7211 7209	,, 7210 ,,	
710·1	220	—	8689 8704 8722 8723	,, 8710 ,,	

Pressure of Bromonaphthalene. Weight = 0·07374 gram.

Pressure reduced to 0°.	Temperature on air thermometer.	Pressure.	
mm.		mm.	
181·75	220°	8855 8890 8879 8940	Mean 8891 mm.
236·6	230	10617 10701 10700 10734	,, 10688 ,,
304·15	240	12783 12801 12811 12850	,, 12811 ,,

Weight = 0·005358 gram.

Pressure reduced to 0°.	Temperature on air thermometer.	Volume.	Pressure.	P.V.	Vapour-density.
mm.		c.c.	mm.		mm.
304·15	240°	1·1652	2139	2492	34·27
,,	,,	1·0237	2389	2446	34·93
,,	,,	0·84417	2851	2407	35·49
,,	,,	0·66563	3512	2338	36·54
,,	,,	0·48769	4578	2233	38·26
,,	,,	0·38234	5612	2145	39·81
,,	,,	0·31251	6604	2063	41·39
,,	,,	0·24254	8043	1950	43·78
,,	,,	0·20747	9006	1869	45·71
,,	,,	0·17233	10295	1774	48·14
,,	,,	0·13714	11930	1637	52·21
—	—	—	12575	—	—
—	—	—	12706	—	—
—	—	—	12811	Mean 12813 mm.	
—	—	—	12816		

Weight = 0·07374 gram.

Pressure reduced to 0°.	Temperature on air thermometer.	Volume.	Pressure.	
mm.		c.c.	mm.	
386·35	250°	—	15077, 15168, 15172, 15222	Mean, 15160.
487·35	260	—	17775, 17910, 17919, 17965	Mean, 17892.
608·75	270	1·1839	19327	Liquid?
,,	,,	1·1661	19447	Liquid present and increasing in amount with decrease of volume.
,,	,,	1·1307	19766	
,,	,,	1·0954	20077	
,,	,,	1·0601	20370	
,,	,,	1·0245	20638	
,,	,,	0·9889	20785	Mean vapour-pressure, 21100.
,,	,,	0·88095	21045	
,,	,,	0·73741	21071	(Obtained graphically).
,,	,,	0·38274	21241	

Weight = 0·07374 gram.

Pressure reduced to 0°.	Temperature on air thermometer.	Volume.	Pressure.	P.V.	Vapour-density.
mm.		c.c.	mm.		mm.
750·5	279·85°	1·1665	20669	24112	52·54
,,	,,	1·1311	21043	23807	53·22
,,	,,	1·0958	21444	23501	53·90
,,	,,	1·0604	21762	23088	54·86
,,	,,	1·0249	22147	22707	55·78
,,	,,	0·98930	22565	22328	56·73
,,	,,	0·95343	22993	21929	57·76
,,	,,	0·91743	23383	21455	59·04
,,	,,	0·88125	23907	21077	60·09
,,	,,	0·84514	24260	20504	61·77
,,	,,	0·86280	24075	20777	60·97
,,	,,	—	24745	Mean 24616 mm.	
,,	,,	—	24655		
,,	,,	—	24447		

Weight = 0·005358 gram.

Pressure reduced to 0°.	Temperature on air thermometer.	Volume.	Pressure.	P.V.	Vapour-density.
mm.		c.c.	mm.		mm.
759·5	280·4°	1·1665	2400	2800	32·91
,,	,,	1·1311	2475	2800	32·92
,,	,,	1·0958	2556	2801	32·89
,,	,,	1·0604	2639	2798	32·93
,,	,,	1·0249	2731	2799	32·91
,,	,,	0·9893	2824	2794	32·97
,,	,,	0·8451	3284	2775	33·20
,,	,,	0·6664	4085	2722	33·85
,,	,,	0·4882	5383	2629	35·06
,,	,,	0·3828	6661	2550	36·14
,,	,,	0·2779	8742	2429	37·93
,,	,,	0·2077	11048	2295	40·15
,,	,,	0·1725	12742	2199	41·92
,,	,,	0·1373	15105	2073	44·43
,,	,,	0·1020	18496	1887	48·84
,,	,,	0·08432	20693	1745	52·79
,,	,,	0·07724	21848	1689	54·57
,,	,,	0·06664	23433	1561	58·99
—	—	—	23891	Very little liquid.	
—	—	—	24556	Mean 24680 mm.	
—	—	—	24741		
—	—	—	24744		

Reduction and Arrangement of Results.

23. *Vapour-pressures.*—As we have already published two papers

on this subject (*Trans. Roy. Soc.*, 1884, 465; and *Chem. Soc. Trans.*, 1885, 42), and have there discussed the results of other observers, we need not reproduce them here. The measurements were there given up to a pressure of 720 mm.; above that pressure the results are new.

We have first to point out an anomalous condition with acetic acid for which we have discovered no parallel in the cases of alcohol and ether. With alcohol and with ether, constant results were obtained, whatever were the relative volumes of liquid and vapour. But with acetic acid condensation takes place before the pressure becomes nearly constant; when a considerable amount of liquid is present, however, pressure remains nearly constant with decrease of volume. It might at first be supposed that this behaviour is due to the presence of air, or some indifferent gas which had originally been dissolved in the liquid; but the complete absence of air is insured by the method of filling, moreover, its absence is demonstrated by the fact that the pressure remains nearly constant until condensation is complete; whereas when air is present, a bubble is left behind, and is not dissolved without a considerable rise of pressure. It has been stated by Wüllner and Grotrian (*Pogg. Ann.*, 11, 545) that the phenomenon is general; this, however, is the first instance in which we have observed it; and, as our work on alcohol and on ether shows no sign of it, we cannot agree with their opinion that it is general. The question may be asked, then—What is the true vapour-pressure? We have taken the mean of four fairly concordant observations when condensation is well advanced. As might be expected, however, the agreement between individual observations is not so good as with alcohol and ether.

24. As with alcohol and ether, a formula of the form recommended by Biot was calculated so as to smooth the results of individual observations, and to afford a means of calculating the values of $\frac{dp}{dt}$. The results of experiment were first smoothed graphically, and five pressures were chosen corresponding with equal intervals of temperature, viz., 0°, 70°, 140°, 210°, and 280°. The corresponding pressures are 3·3 mm., 136 mm., 1414 mm., 7237 mm., and 24620 mm. The constants for the formula—

$$\log p = a + b\alpha^t \times c\beta^t,$$

are $a = 6{\cdot}7003112$ $\quad \log \alpha = \bar{1}{\cdot}998815139,$

$\log b = 0{\cdot}6879733$ $\quad \log \beta = \bar{1}{\cdot}994508740,$

$\log c = 0{\cdot}1162143,$

b and c are both negative.

We now give a table showing the results obtained experimentally, and those calculated by the above formula. The results previously

given (*loc. cit.*) which were obtained graphically are under the heading of found numbers. The value for 0° is extrapolated from 2·7°, where the last observation with the liquid acid was made.

25. Vapour-pressures of Acetic Acid.

Temperature.	Pressure. Found.	Pressure. Calculated.	Temperature.	Pressure. Found.	Pressure. Calculated.
	mm.	mm.		mm.	mm.
0°	3·5	3·30	150°	1846	1846·8
10	6·34	6·38	160	2370	2381·6
20	11·80	11·73	170	3031	3035·2
30	19·9	20·61	180	3819	3826·4
40	34·0	34·77	190	4750	4775·5
50	56·2	56·56	200	5860	5904·7
60	88·3	88·94	210	7210	7237·9
70	137·1	136·0	220	8801	8800·1
80	202·1	202·3	230	10688	10619·0
90	292·8	293·7	240	12794	12724·0
100	416·5	417·1	250	15159	15144·0
110	582·6	580·8	260	17892	17913·0
120	—	794·0	270	21060	21063·0
130	1040·0	1067·6	280	24603*	24629·0
140	1381·0	1414·0	—	—	—

* Calculated from observations at 279·85° and at 280·4°.

Rate of Increase of Pressure per Unit Rise of Temperature.

26. The values of these constants, $\frac{dp}{dt}$, were calculated in the following manner:—The pressures at one-tenth of a degree above, and at one-tenth of a degree below any given temperature were calculated, and the difference multiplied by 5. The results are given in the annexed table.

Temperature.	$\frac{dp}{dt}$.	Temperature.	$\frac{dp}{dt}$.	Temperature.	$\frac{dp}{dt}$.
	mm.		mm.		mm.
0°	0·227	100°	14·20	200°	123·1
10	0·404	110	18·75	210	144·3
20	0·686	120	24·20	220	168·5
30	1·120	130	30·80	230	195·2
40	1·750	140	38·70	240	225·3
50	2·645	150	48·15	250	258·5
60	3·895	160	59·00	260	294·3
70	5·550	170	72·00	270	334·9
80	7·78	180	86·85	280	378·5
90	10·60	190	103·5	—	—

Expansion of Liquid Acetic Acid.

27. As all the observations, with few exceptions, have been made at definite intervals of temperature, the tables already given need not be reproduced.

But it appears advisable to give here a comparison of the results obtained by us with those of other observers. This, however, is difficult. Kopp (*Annalen*, **64**, 216, and **92**, 11; and *Pogg. Ann.*, **72**, 1, 223) gives a series of determinations of the expansion of acetic acid; but it is evident, on reviewing his results, that the sample of acid used by him is not quite comparable with ours. The boiling point of our acid at 760 mm., calculated from a direct observation at 765·2 mm., is 118·5°; and from our constants, with Biot's formula, 118·55°; whereas Kopp's sample boiled at 117·3° at 760 mm. The sp. gr. of Kopp's sample at 0° (probably extrapolated) was 1·0801, while ours, also extrapolated, is 1·0697. Nevertheless, the rate of expansion between 30° and 120° is nearly the same in both cases, and we have therefore taken the mean of three comparisons at 30°, 40°, and 70°, to reduce Kopp's values, in which the volume at 0° is taken as unity, to the volumes of 1 gram. We append a comparison of the volumes obtained by him and by us.

Temperature.	Volume of 1 gram.		Temperature.	Volume of 1 gram.	
	Kopp.	R. and Y.		Kopp.	R. and Y.
0°	0·9323	0·9348	70°	1·0052	1·0052
10	0·9422	0·9440	80	1·0168	1·0168
20	0·9521	0·9532	90	1·0288	1·0290
30	0·9622	0·9623	100	1·0415	1·0418
40	0·9725	0·9724	110	1·0547	1·0545
50	0·9831	0·9828	120	1·0685	1·0682
60	0·9940	0·9940	—	—	—

At higher temperatures, however, Kopp's formula,

$$v = 1 + at + bt^2 + ct^3,$$

where the logarithms of a, b, and c are $\bar{3}{\cdot}02408$, $\bar{7}{\cdot}26300$, and $\bar{9}{\cdot}98423$, as might be expected, ceases to represent the results. For instance, at 200° the volume calculated is 1·2081, and found by us 1·2117; and at 208°, 1·4189, compared with 1·5172.

28. Perkin has recently made determinations of the sp. gr. of acetic acid (Trans., 1884, 481). His sample, however, did not show a constant boiling point. The specific volume found by him at 15° was

0·9468, and at 25°, 0·9570. We find 0·9482 and 0 9579 at these temperatures.

A review of the determinations of the sp. gr. of acetic acid is given by Lossen (*Annalen*, **214**, 97).

Vapour-densities of Acetic Acid.

29. The results actually obtained by experiment are represented by circles on Plate I. The vapour-pressure corresponding with each isotherm having been marked off, curves were drawn to pass through the experimental points, which cut the horizontal lines representing vapour-pressures at the condensation points. The curve which passes through these points of intersection gives the densities of the saturated vapour at any pressure.

In Plate II, the variation of vapour-density with alteration of temperature, is shown, at constant pressure. The diagram was constructed by reading off from Plate I, and from a similar diagram giving results at higher temperatures, the densities of vapour corresponding with temperatures of observation at definite pressures. These were then plotted to give isobaric curves. The temperatures corresponding with different vapour-pressures are here represented by straight lines, and the points of intersection of the isobars with these lines again represent the densities of saturated vapour, but now referred to definite temperatures. It will be seen on inspection that Plate II includes the whole of our observations, whilst Plate I represents the lower portion in detail. It has already been stated in Section 23, that condensation begins before the vapour-pressure is attained; this is seen on the diagram (Plate I) where the experimental results, near the saturation point, do not correspond with the lines drawn.

30. The table (p. 808) shows the vapour-densities at definite temperatures and pressures.

31. The vapour-densities of acetic acid at pressures below an atmosphere have been made the subject of experiment by Naumann (*Annalen*, **155**, 325). Naumann's measurements were made in a Hofmann's tube, but without any arrangement for controlling pressure; the pressure adjusted itself according to the temperature and the weight of substance taken. His temperatures, also, have confessedly no great claim to accuracy, for the jacketing vapours used at temperatures between 100° and 185° (which were obtained by water-vapour and aniline-vapour boiling at a pressure which he does not give), were those of various mixtures of hydrocarbons. His results, therefore, can only claim to be approximate; as they serve, however, to corroborate our results, we give a few of his measurements for the sake of comparison (p. 809).

Temperatures.	Pressures in millimeters.											
	20	40	100	300	500	1,000	2,000	5,000	10,000	16,000	20,000	24,000
40°	54·22											
50	50·62	53·61										
60	47·04	50·38										
70	43·55	47·12	51·21									
80	40·45	43·86	48·08									
100	35·63	37·92	41·81	48·50								
120	32·75	34·01	36·50	42·79	46·71							
140	31·32	32·12	33·72	38·05	41·42	46·81						
160			32·10	34·77	36·88	41·80	47·81					
180			31·17	32·66	34·01	37·39	42·58					
200							38·64	47·99				
220							35·82	42·39				
240							34·00	38·79	47·60			
260							32·89	36·39	42·80	53·00		
280							32·21	34·66	39·10	45·45	51·34	60·70

Pressure. mm.	Temperature.					
	Naumann. 78°	R. and Y. 78°	Naumann. 100°	R. and Y. 100°	Naumann. 120°	R. and Y. 120°
100	45·7	48·75	40·5	41·81	35·1	36·5
180	50·0	51·95	43·9	45·00	38·8	39·56
300	—	—	47·2	48·50	42·4	42·79
400	—	—	49·9	50·64	44·7	44·99

Pressure. mm.	Temperature.			
	Naumann. 140°	R. and Y. 140°	Naumann. 185°	R. and Y. 185°
100	32·0	33·72	—	—
180	34·4	35·92	30·9	31·52
300	37·2	38·05	32·0	32·28
400	39·4	39·83	32·8	32·9

32. Horstmann also has made experiments on the vapour-density of acetic acid. In his first paper (*Ber.*, **2**, 299), he suggested that a difference should exist between the forms of the curves representing the densities of the saturated vapour in the case of a true dissociating substance and of acetic acid. He supposed that the density of dissociating substances increases with fall of temperature, but that in the case of acetic acid it decreases; and in his second paper (*Ber.*, **3**, 78) he gives experimental determinations of the density of the saturated vapour, which, using his calculations, confirm his view, although they are in direct contradiction to the experimental evidence adduced by Bineau (*Annalen*, **60**, 157) and by us. Horstmann's experiments were made by passing air over acetic acid kept at a known temperature, and estimating by absorption with caustic potash the amount of acid carried over. He calculated the density by means of the formula

$$D = \frac{G(P - p)}{V_0 . p . 0{\cdot}001293 \times 14{\cdot}435},$$

where G is the weight of acid, P the atmospheric pressure, p the vapour-pressure of acetic acid, and V_0 the volume of air reduced to normal temperature and pressure.

33. But in calculating, he employed Landolt's pressures, which at the lowest temperatures are nearly double those obtained by Regnault and by us. On recalculating his results with true vapour-pressures, it is found that there is a tendency for the density of the saturated

vapour to rise, instead of to fall, with decrease of temperature; though the results are not sufficiently concordant to be plotted in the form of a curve.

34. We append these results as given by him, and, as recalculated, converting his specific gravities into vapour-densities compared with hydrogen. For temperatures below 17°, the vapour-pressures of the solid acid were employed.

Temperature.	Pressure.		Density.	
	Landolt.	R. and Y.	Landolt.	R. and Y.
	mm.	mm.		
12·4°	13·5	6·40	27·29	58·27
12·7	13·7	6·51	28·29	60·11
14·7	15·1	7·85	25·70	49·92
15·6	15·6	8·60	28·58	52·33
17·4	16·8	10·00	30·31	51·39
20·2	19·0	11·80	32·91	53·51
21·5	20·4	12·72	32·33	52·39
22·6	21·2	13·50	33·06	52·46
25·0	23·5	15·35	34·93	54·08
26·5	25·0	16·60	33·49	51·01
27·6	26·5	17·55	35·51	54·28
33·3	33·4	23·0	37·24	54·85
38·5	41·5	31·2	39·26	52·97
38·5	41·5	31·2	40·27	52·97
44·6	53·1	42·0	39·70	50·98
48·7	63·0	51·5	43·02	53·50
51·1	69·0	58·0	45·62	55·14
59·9	97·0	88·3	45·04	50·13
62·9	109·2	99·0	44·89	50·29
63·1	110·0	100·5	46·05	51·14

These figures speak for themselves as to the value to be attached to Landolt's and Horstmann's experimental work.

35. Bineau's determinations are as follows:—

Temperature.	Pressure.	Density.	Temperature.	Pressure.	Density.
	mm.			mm.	
12°	2·44	54·9	28·0°	10·03	54·1
19	2·60	52·8	35·0	11·19	52·5
22	2·70	51·4	36·5	11·32	52·3
12	5·23	56·6	20·0	4·0	54·0
20	5·56	54·4	,,	5·6	54·4
24	5·75	53·4	,,	8·5	56·0
30	6·03	52·0	,,	10·0	57·2
20	8·55	56·0	30·0	6·0	52·0
22	8·64	55·6	,,	10·7	53·8
20·5	10·03	57·0	—	—	—

The series at 20° constitutes an isothermal obtained by Bineau from his observations. A straight line drawn through these points, to meet the vapour-pressure line, would give the density of the saturated vapour equal to about 58·4; whilst our results would give, if extrapolated, about 59·3, a very close agreement. Bineau's vapour-pressures also agree well with ours.

36. We next give a table of the densities of the saturated vapour, read from the curve on Plate II. It should be borne in mind that on account of the abnormal behaviour of acetic acid while condensing, these numbers must be regarded as minimum values, although above 40° it is probable that they are nearly correct:—

Temperature.	Density.	Temperature.	Density.	Temperature.	Density.
20°	59·3	110°	50·60	200°	51·06
30	57·7	120	50·32	210	51·59
40	56·2	130	50·16	220	52·26
50	55·0	140	50·08	230	53·13
60	53·77	150	50·06	240	54·24
70	52·76	160	50·12	250	55·62
80	52·00	170	50·22	260	57·28
90	51·40	180	50·40	270	59·43
100	50·95	190	50·64	280	62·62

37. *Latent Heats of Vaporisation.*

From these densities of saturated vapour, the heats of vaporisation were calculated by the formula

$$L = (S_1 - S_2) \cdot \frac{dp}{dt} \cdot \frac{t}{J},$$

where $L =$ heat of vaporisation; $S_1 =$ volume of 1 gram of saturated vapour; $S_2 =$ volume of 1 gram of liquid; $\frac{dp}{dt} =$ rate of increase of pressure in absolute units (grams per square centimetre) per unit rise of temperature at the given temperature; $t =$ absolute temperature; and $J =$ the mechanical equivalent of heat (42500).

The data and results are given in the following table (p. 812).

The heat of vaporisation of acetic acid has been measured at its boiling point under atmospheric pressure by Favre and Silbermann, and by Berthelot. The former (*Annalen*, **64**, 186) used acid boiling at 120°, and found the heat of vaporisation to be 101·9 cals.; and Berthelot (*Essais de Mechan. Chim.*, **1**, 418) gives the number 120·8 cals. Our value at 120° is 92·71. It appears probable that

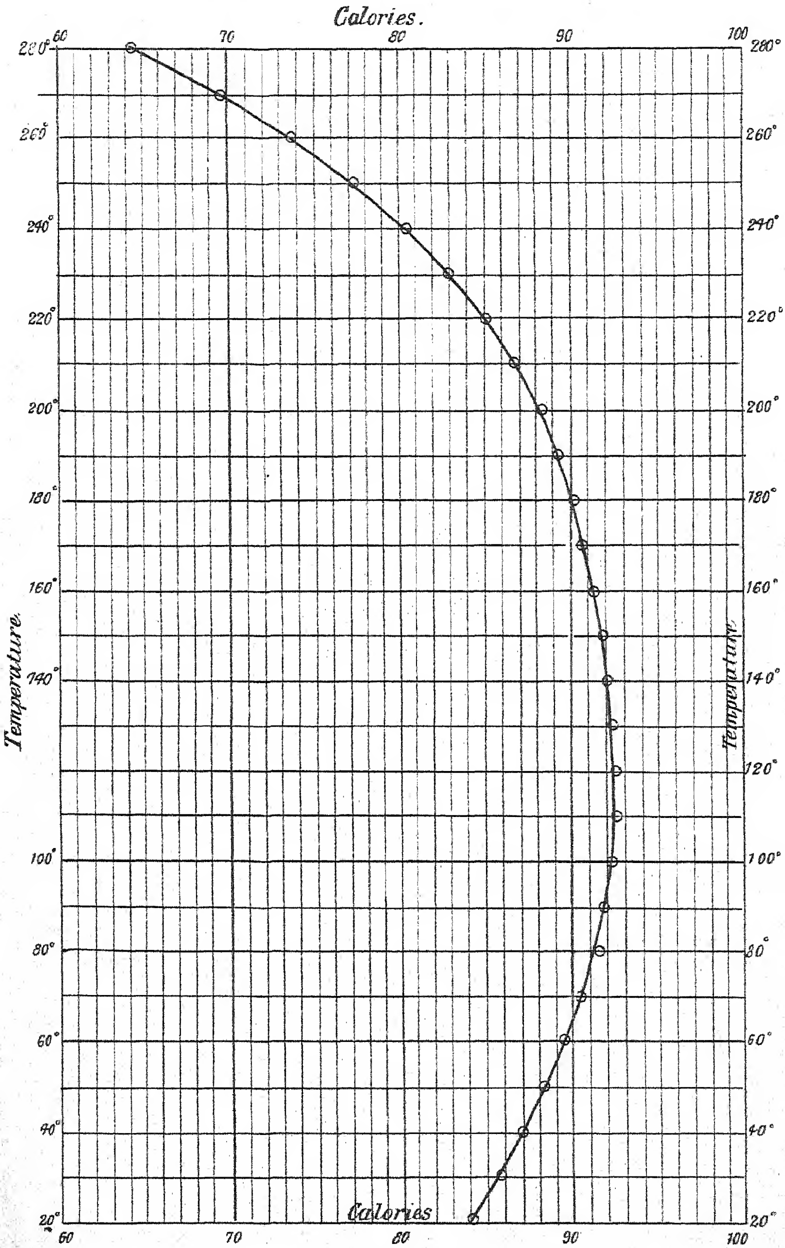
Temperature.	S_1.	$(S_1 - S_2)$.	$\frac{dp}{dt}$.	$\frac{t}{J}$.	L.
20°	13080	13079	0·933	0·00689	84·05
30	7911	7910	1·523	0·00713	85·88
40	4970	4969	2·379	0·00736	87·02
50	3226	3225	3·596	0·00760	88·14
60	2164	2163	5·296	0·00783	89·69
70	1486	1485	7·546	0·00807	90·43
80	1043	1042	10·58	0·00831	91·59
90	747·5	746·5	14·41	0·00854	91·88
100	545·6	544·6	19·31	0·00878	92·32
110	405·1	404·0	25·49	0·00901	92·79
120	305·7	304·6	32·90	0·00925	92·71
130	233·9	232·8	41·88	0·00948	92·42
140	181·3	180·2	52·62	0·00972	92·16
150	142·2	141·1	65·47	0·00995	91·91
160	112·7	111·6	80·22	0·01019	91·22
170	90·29	89·14	97·89	0·01042	90·92
180	72·97	71·80	118·1	0·01066	90·38
190	59·48	58·29	140·7	0·01089	89·32
200	48·74	47·53	167·4	0·01113	88·54
210	40·19	38·95	196·1	0·01136	86·82
220	33·32	32·06	229·1	0·01160	85·20
230	27·72	26·43	265·3	0·01184	83·03
240	23·12	21·80	306·3	0·01207	80·59
250	19·32	17·95	351·5	0·01231	77·65
260	16·17	14·76	400·1	0·01254	74·07
270	13·51	12·05	455·3	0·01278	70·12
280	11·21	9·69	514·6	0·01301	64·88

the higher numbers found directly were due to want of purity of the samples employed. With alcohol and with ether, there was a close concordance between our results and the direct observations by Andrews, Regnault, and Favre and Silbermann. With these substances, also, the heats of vaporisation do not rise with fall of temperature; but with acetic acid there is a rise from 280° downwards, reaching a maximum at about 110°, and then a continuous fall. This is shown graphically in Plate III.

For the sake of comparison, small diagrams showing the relation of the vapour-density of alcohol to temperature and pressure have been inserted. In Plate IV, isothermals at comparatively low pressures are given; the trend of the curve below 110° is characteristic of stable substances. In Plate V, a large portion of the isobaric diagram is given. At higher temperatures than are shown in the diagram, the curve becomes more and more horizontal until the critical temperature and pressure are reached. The fundamental difference between these diagrams and those exhibiting similar relations of acetic acid is very striking.

Journ. Chem. Soc. October 1886. Plate III.

HEATS OF VAPORIZATION OF ACETIC ACID.



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Journ. Chem. Soc. October 1886.

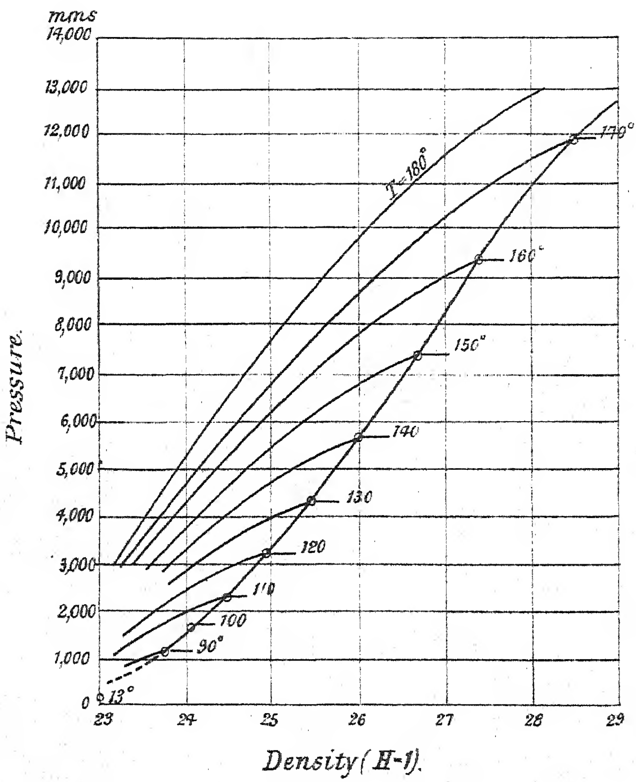
Plate IV

DENSITIES OF SATURATED AND UNSATURATED VAPOUR OF ALCOHOL.

(H = 1 at t° and p mms.)

(Lower portion of diagram only).

ISOTHERMS.



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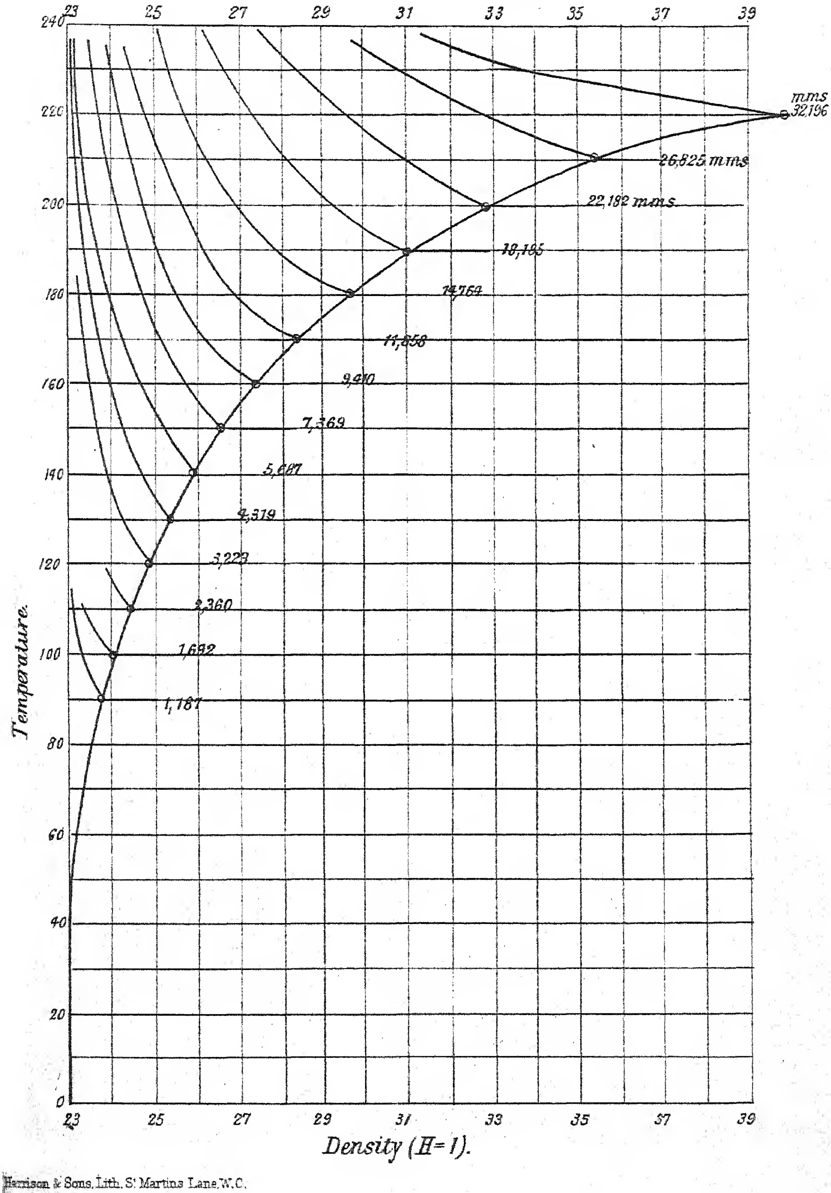
DENSITIES OF SATURATED AND UNSATURATED VAPOUR OF ALCOHOL.

ISOBARS.

(H = 1 at t° and p mms.)



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LXXVI.—*Trimethyldiethylamidobenzene.*

By R. F. Ruttan, B.A., M.D., Lecturer on Chemistry in McGill University, Montreal.

In 1872 A. W. Hofmann (*Ber.*, **5**, 720) observed that at high temperatures the halogen salts of secondary, tertiary, or even quaternary bases of the aromatic series are converted into the salts of their isomeric primary bases by a transfer of the fatty radicles from the side-chain to the nucleus. Thus the hydriodide of monomethylaniline at a high temperature becomes converted into the corresponding salt of toluidine :—

$$\left.\begin{matrix} C_6H_5 \\ CH_3 \\ H \end{matrix}\right\} NHI = \left.\begin{matrix} C_6H_4(CH_3) \\ H \\ H \end{matrix}\right\} NHI.$$

This reaction is now developed technically, and is largely employed by the *Gesellschaft für Anilinfabrik in Berlin* for the preparation of the higher homologues of aniline, especially pseudocumidine. On submitting the latter to his reaction, Hofmann has recently obtained an interesting substance, pentamethylamidobenzene, the first homologue of aniline in which all the hydrogen-atoms of the benzene nucleus are replaced by fatty radicles (*Ber.*, **18**, 1821). It is known that the transfer of radicles from the side-chain to the benzene-ring is by no means confined to the methyl series. Hofmann himself has shown that the phenyl-groups in aniline may be ethylated or amylated in the same manner. It seemed of some interest, however, to ascertain how far the presence of methyl-groups in the phenyl-group of aniline would promote or retard the introduction of other radicles of different composition. In order to decide this question, I began by submitting pseudocumidine to the action of ethyl alcohol, with the view of obtaining a primary monamine in which the phenyl-group should contain three methyl- and two ethyl-groups, that is of the formula $C_6(CH_3)_3(C_2H_5)_2{\cdot}NH_2$. The first step in the production of this compound is the preparation of ethylcumidine. For this purpose dry cumidine hydrochloride was mixed with somewhat more than the theoretical quantity of ethyl alcohol, and the mixture heated in a closed tube at 120—130° for four hours. The product was found to be the hydrochloride of the ethylated cumidine, together with some ether formed during the reaction. Excess of alkali added to this product caused the ethylated cumidine and the ether to rise to the surface, and they were then easily removed and separated.

Distillation very readily removes the ether and leaves a basic residue, which comes over between 220° and 230°.

It is worthy of note that this method of ethylating cumidine yields better results than the usual one of digesting the base with a haloïd ether, and then separating the secondary amine by excess of alkali. Moreover, the employment of the more costly iodide is avoided.

The mixture of secondary and tertiary bases thus obtained is sealed up in tubes with about an equal weight of ethyl iodide, and heated to a temperature of 260° to 280° for eight or ten hours. If the operation be successful, the tubes, on cooling, contain a dark-red jelly-like mass, which cannot be poured out. This consists of the new base mixed with other bases, a small quantity of some liquid, aromatic hydrocarbons, and a tarry substance. The hydrocarbons are removed by distillation with steam, and the residue filtered and treated with concentrated alkali, when a thick reddish strongly basic oil rises to the surface. This is fractionally distilled, and the part which comes over between 285° and 290° is retained and treated with hydrochloric acid, when a very insoluble hydrochloride, crystallising in groups of needles, is at once formed. These are not soluble in cold water to any appreciable extent, and only very slightly soluble in boiling water, but easily soluble in alcohol.

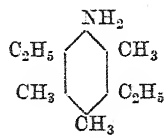
After one or two recrystallisations, this salt was obtained in a state of purity. Analysis proved it to be the hydrochloride of trimethyldiethylamidobenzene, $C_6(CH_3)_3(C_2H_5)_2{\cdot}NH_2,HCl$, which requires the following values:—

			Experiment.		
		Theory.	I.	II.	III.
C_{13}	156·0	67·20	66·82	—	—
H_{22}	22·0	9·65	9·72	—	—
N	14·0	7·47	—	—	—
Cl	35·5	15·68	—	15·6	15·573
	227·5				

The free trimethyldiethylamidobenzene obtained from this salt by the action of an alkali is a liquid boiling between 288—290°. It has a sp. gr. of 0·971, is quite colourless when first set free, and has a faint odour. After a time, it becomes thick and dark coloured.

The hydrochloride does not yield a well crystallised platinochloride, but with palladium chloride it gives a beautiful green palladium salt in feathery crystals. The acetate and sulphate crystallise in needles and are very soluble. The oxalate is very sparingly soluble, and consists of large prisms. The acetyl compound, easily obtained by the action of acetic anhydride, crystallises in rosettes of needles and melts at 182°.

The primary character of the base is at once proved by its giving Hofmann's isonitrile reaction with alkali and chloroform. As proved by the researches of Froelich (*Ber.*, **17**, 1801 and 2073), the methyl-groups in pseudocumidine hold the positions 2, 4, and 5, that of the amido-group being 1. As there are thus only two places vacant for the ethyl-groups, the substance I have described is represented as follows:—



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LXXVII.—*On the Action of Bromine on Phosphorus Trichloride.*

By A. L. Stern, Scholar in the Chemical Laboratory of the Mason College, Birmingham.

The action of bromine on trichloride of phosphorus was first investigated by Gladstone (*Phil. Mag.*, **35**, 1849, 353—354), when attempting to form a compound of phosphorus containing both halogens, that is, a chlorobromide of phosphorus. He found that when bromine was poured into phosphorus trichloride, it sank to the bottom and two layers were formed, the upper consisting of a solution of bromine in the trichloride and the lower of a solution of the trichloride in bromine. These two layers could not be made to mix, but on adding a little iodine combination immediately took place with development of much heat, and on cooling red crystalline masses separated, resembling phosphorus pentabromide with excess of bromine. These crystals having been freed as far as possible from the mother-liquor, were analysed by decomposing them with water and precipitating with silver nitrate. Their percentage composition was found to be—

Bromine	88·6
Chlorine	6·4
Phosphorus (by difference)	5·0

This Gladstone regarded not as a compound of both halogens, but

merely as phosphorus pentabromide contaminated with a little chloride, the pentabromide requiring—

Bromine..............	92·45 per cent.
Phosphorus	7·55 ,,

The reaction is probably

$$PCl_3 + Br_5I = PBr_5 + ICl_3.$$

Gladstone also tried other methods for forming the chloro-bromide but without success.

Wichelhaus (*Annalen*, Supp. **6**, 277) states that phosphorus trichloride and bromine combine with development of heat, and that the product when cooled by a powerful freezing mixture deposits crystals, which he assumed to be PCl_3Br_2. On exposure to the ordinary temperature, however, these melt, and the liquid separates into two layers.

Friedel and Ladenburg (*Bull. Soc. Chim.*, **8**, 1867, 146) used a mixture of PCl_3+Br_2, and found it reacted as if it was PCl_3Br_2.

Michaelis (*Ber.*, **5**, 9) found that the chlorobromide was stable at ordinary temperatures. By exposing a mixture of the trichloride with bromine in the proportion $PCl_3 : Br_2$ in a tube for some time to a winter temperature, he obtained the compound PCl_3Br_2 (the analysis gave PCl_3Br_2 + 5·2 per cent. PCl_3), decomposing into PCl_3 and Br_2 at 35°. On placing crystals of this or even of some of the mother-liquor in a mixture of phosphorus trichloride and bromine, the lower layer immediately solidified, the compound PCl_3Br_4 separating out, just as a supersaturated solution solidifies when a crystal of the salt is dropped into it. On treating this compound with PCl_3 he found it to be unaltered.

Prinvault (*Compt. rend.*, **74**, 868) found that a homogeneous liquid was obtained on gradually adding bromine to phosphorus trichloride. On heating this on a water-bath until bromine was no longer evolved, a red liquid was left, which crystallised at −4° or − 5°, forming brown oily needles, and it is stated that this compound can be distilled unchanged below 90°, producing a colourless vapour of the formula PCl_3Br_8. Quick distillation above 90°, however, decomposes it, crystals of PCl_2Br_7 being obtained in the receiver; if this is dissolved in cold PCl_3, and the solution boiled, yellow crystals of PCl_4Br separate on cooling.

Prinvault also obtained PCl_3Br_4 thus:—

$$PCl_3Br_8 + PCl_3 = PCl_2Br_7 + PCl_4Br,$$
$$PCl_2Br_7 + PCl_4Br = 2PCl_3Br_4.$$

Michaelis (*Ber.*, **5**, 414) has repeated the above experiments, and

obtained different results. When $2Br_2$ was added to PCl_3 there appeared after strong heating a homogeneous oily liquid, which on cooling crystallised, giving brown needles with a green reflex, of the composition approximately represented by the formula PCl_3Br_8; he found that this compound could not be distilled without decomposition, and that its vapour was of the colour of bromine. Michaelis considers these compounds to have a similar constitution to PCl_5,ICl and PCl_3,Fe_2Cl_6; while Prinvault holds them to be compounds of PBr_5 with BrCl.

With a view to the more complete investigation of this reaction, the following experiments were performed.

Phosphorus trichloride was mixed with bromine (free from iodine) in various proportions, the mixture allowed to stand, and the crystals which were deposited were analysed.

Three series of experiments were performed.

Phosphorus trichloride and bromine were run from two burettes into small stoppered bottles; heat was developed, and on cooling crystals were deposited; in order to obtain them free from the mother-liquor, the contents of the bottles were poured into funnels, the stems of which were plugged with asbestos, and the funnels were then placed in a closed vessel over soda-lime. In order to obtain them even approximately free from the mother-liquor, they had to drain for at least 24 hours; during that time decomposition seemed to take place, and on attempting to transfer them from the funnel to a small weighing tube, they deliquesced so rapidly that it was useless to analyse them.

A process had therefore to be devised by means of which the crystals could be freed from the mother-liquor and weighed without exposing them to the atmosphere. This was done as follows.

A glass tube about $\frac{1}{4}$ inch in diameter and 10 inches long, was drawn out into a narrow neck at one end and the bottom of this sealed off. The narrow neck having been plugged with asbestos, measured quantities of phosphorus trichloride and bromine were run in at the top from a dry burette, the lower sealed part of the tube being occasionally cooled to moderate the heat produced by the reaction, otherwise the PCl_3 boiled.

The tube was then sealed off at the top. In order to separate the crystals which formed on cooling, the two ends of the tube were broken and a current of air dried by sulphuric acid was drawn through the tube by means of a filter-pump in communication with the lower end. When the mother-liquor had been drawn off, both ends of the tube were re-sealed, and the whole weighed.

The crystals were then dissolved in solution of sulphurous acid by breaking off one end of the tube under the surface of the solution, and allowing the liquid to rise in the tube. The tube was then

washed, dried, and re-weighed, together with the ends broken off. The difference in weight gave the amount taken for analysis.

The solution was made up to a definite volume, and to a measured quantity of this, decinormal silver nitrate added as long as a precipitate formed. The phosphorus was determined by difference.

The trichloride and the bromine were mixed in four different proportions.

(i.) $PCl_3 : Br_2$.—Heat was developed on mixing, and two layers were formed, the lower dark-red and the upper light-red; after standing a few hours the lower one suddenly solidified to a brick-red crystalline mass.

(ii.) $PCl_3 : 2Br_2$.—More heat was developed on mixing than in the former case, and a homogeneous red liquid was formed; a quantity of dark-red crystals separating out on cooling.

(iii.) $PCl_3 : 3Br_2$.—A considerable amount of heat was developed on mixing, and a homogeneous red liquid was formed; on sealing up and shaking, a quantity of dark-red crystals separated.

In each of these three experiments, the mother-liquor was drawn off on the following day; temperature about 13°.

(iv.) $PCl_3 : 6Br_2$.—A considerable amount of heat was developed on mixing; a homogeneous red liquid was formed, and dark-red crystals separated out on cooling. These were left in contact with the mother-liquor for 31 days, in order to see if all the chlorine could be displaced by prolonged contact with excess of bromine. This, however, was not the case.

As the phosphorus in this series was merely estimated by difference, and as no precautions were taken to eliminate moisture from the bromine, or phosphorous acid from the trichloride, and as the use of asbestos as a filtering material might be open to objection, a second series of analyses was performed. In this series, the bromine was first tested for iodine, and found to be free from it, then shaken up, and left in contact with strong sulphuric acid, and finally distilled into a dry tube similar in construction to the one previously described, except that the asbestos was replaced by platinum gauze fused into the tube. The phosphorus trichloride was also distilled directly into the tube.

In the former series, the liquids were measured from a burette, in this one by marking lengths on the tubes proportional to the required volume.

The mode of analysis was slightly modified; the crystals were decomposed as before by dilute sulphurous acid, and the solution made up to a definite volume. To determine the chlorine and bromine, silver nitrate was added to a portion of the solution and the precipitate of Ag(Cl,Br) weighed; a portion of this was then transferred to a

weighed bulb-tube and heated in a stream of chlorine until the weight was constant. From these results, the quantity of chlorine and bromine could be calculated. To another portion of the solution, bromine in excess was added to oxidise the phosphorous acid to phosphoric acid, and the phosphorus estimated from the weight of magnesium pyrophosphate obtained on precipitation with magnesia mixture.

The bromine and trichloride were mixed in approximately the same proportions as in Series I, with the exception of the first and last experiments.

(i.) $PCl_3 : Br$.—Two layers were formed; but only a small quantity of crystals separated at 4°; these were insufficient in quantity to analyse.

(ii.) $PCl_3 : Br_2$.—Two layers were formed, and a small quantity of crystals separated at 4°. The mother-liquor was drawn off at this temperature, after the mixture had stood 16 days at the summer temperature. The crystals were light red.

(iii.) $PCl_3 : 2Br_2$.—A homogeneous mixture was formed, and a crop of small light-red crystals separated out at the ordinary summer temperature; the mixture was cooled to 4° when a second crop of light-red needle-shaped crystals separated. The mother-liquor was then drawn off.

A second quantity of bromine and PCl_3 was mixed in approximately the same proportion. After this had stood for one day at the summer temperature, the mother-liquor was drawn off; the crystals were light red, and decomposed on keeping.

(iv.) $PCl_3 : 3Br_2$.—The mixture solidified at 4°; on standing for three days at the summer temperature some crystals were deposited, the mother-liquor was then drawn off.

(v.) $PCl_3 : 4Br_2$.—After standing a few hours this was cooled to 4°, when it solidified; the temperature was then gradually raised to 15° and the liquid portion drawn off: the substance thus obtained solidified on cooling with ice to a brick-red mass, commenced to darken at 10°, and fused at 13—17° to a dark-red liquid.

The following conclusions may now be considered as established:—

(i.) When bromine is added to phosphorus trichloride, two atoms of bromine may be made to unite with one molecule of the chloride, forming the chlorobromide, PCl_3Br_2 (Michaelis); when more bromine is added one atom of chlorine in this is displaced by bromine, forming PCl_2Br_3 (see Table II, Series II, No. 1, and Series I, No. 2). Still more bromine being added, this compound unites with part of it, forming PCl_2Br_5 (Table II), and at a lower temperature with still more bromine.

(ii.) The number of atoms of halogen with which one atom of

TABLE I.

		PCl_3Br_2.	PCl_3Br_4.	PCl_3Br_6.	PCl_3Br_8.	PCl_3Br_{12}.	
Calculated composition of mixtures	P Cl Br	10·42 35·80 53·78	6·78 23·28 69·94	5·02 17·25 77·73	3·99 13·70 82·31	2·82 9·70 87·48	— — —
Temp. 13—15° C.		Mixture stood one day.	Mixture stood one day.	Mixture stood one day.		Mixture stood 31 days.	
Crystals, Series I (phosphorus by difference)	P Cl Br	10·89 24·64 64·47	10·12 15·66 74·22	8·25 13·31 78·44	— — —	5·55 9·83 84·62	— — —
		Mixture stood 16 days at summer temp., the mother-liquor was then drawn off at 4°.		Stood three days at summer temp., the mother-liquor was then drawn off at that temp.	—	—	$PCl_3 + 2Br_2$ stood 1 day at summer temp., the mother-liquor was then drawn off at that temp.
Crystals, Series II	P Cl Br	8·82 23·26 69·15	7·77 14·78 78·10	6·08 11·79 83·34	4·19 12·02 84·34	— — —	6·62 14·97 79·17
	—	101·23	100·65	101·21	100·55	—	100·76

TABLE II.—*Atomic Proportions.*

Mixture	P Cl Br	1 3 2	1 3 4	1 3 6	1 3 8	1 3 12
Crystals, Series I ...	P Cl Br	1 2·03 2·29	1 1·35 2·84	1 1·41 3·68	— — —	1 1·55 5·91
Crystals, Series II ..	P Cl Br	1 2·30 3·04	1 1·66 3·89	1 1·69 5·31	1 2·50 7·80	— — —

Mixture	P Cl + Br	1 5	1 7	1 9	1 11	1 15
Crystals, Series I ...	P Cl + Br	1 4·32	1 4·19	1 5·09	— —	1 7·46
Crystals, Series II ..	P Cl + Br	1 5·34	1 5·55	1 7·00	1 10·30	— —

phosphorus can combine depends on the temperature: thus phosphorus in presence of 15 atoms of halogen at temperature 13—15° can combine with only 7 atoms, whereas P in the presence of 11 atoms of halogen united with 10 atoms to form a compound dissociating above 10°.

(iii.) All the chlorine in the trichloride cannot be displaced by the unaided action of bromine, even if such a large excess as 12 atoms of bromine to 1 mol. of PCl_3 be allowed to react for a month (Series I, No. 4); the presence of a small quantity of iodine, however, will enable a much larger quantity of the chlorine to be displaced (Gladstone).

Michaelis regards the chlorobromides in question as molecular compounds of PCl_3 with ClBr, whilst Prinvault considers them to be molecular compounds of PBr_5 with ClBr. Michaelis's view is, however, now scarcely tenable, as it has been shown above that the Cl in PCl_3 may be partly displaced by bromine; Prinvault's view also does not seem tenable, as compounds have been obtained with less than 5 atoms of bromine.

It has been shown that the compounds containing the largest amount of halogen are decomposed at ordinary temperatures, whilst those containing less halogen are stable at this temperature, the compound PCl_3Br_2 being indeed stable below 35° (Michaelis); and as it is also known that phosphorus pentachloride is decomposed on vaporisation into PCl_3 and Cl_2, it would seem that the valency of phosphorus in

these compounds is a function of the temperature, increasing as the temperature falls; and that these compounds are simply compounds of phosphorus with varying quantities of halogen.

In conclusion, I must express my thanks to Dr. Tilden for his kind and valuable help.

LXXVIII.—*The Electrolytic Preparation of Vanadious Sulphate.*

By J. T. Brierley, Dalton Chemical Scholar, Owens College.

Professor Roscoe observed that when a solution of vanadium trioxide was prepared by reducing the higher oxides dissolved in dilute sulphuric acid, the resulting liquid had sometimes a brown and sometimes a green colour. The brown-coloured liquid is usually obtained when a solution of vanadium dioxide from which the excess of acid has been removed by zinc, is allowed to absorb oxygen from the air, being thereby converted into V_2O_3. That these two compounds are of the same degree of oxidation has also been shown by Roscoe.

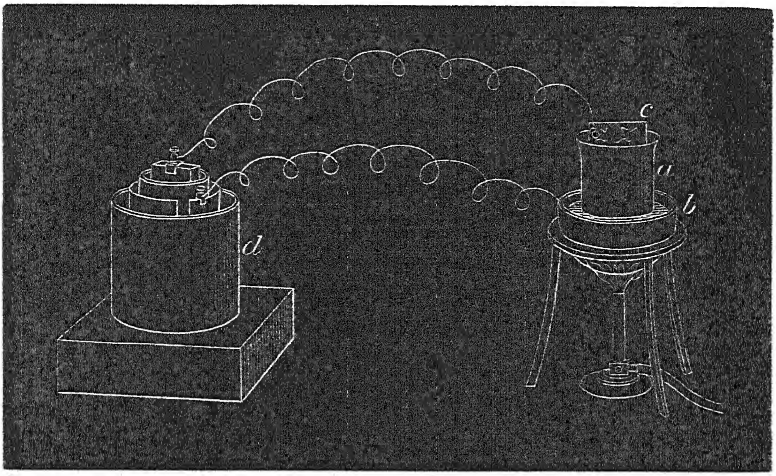
These experiments were repeated very carefully, and it was found that the green trioxide solution could be at once converted into the brown by the addition of zinc oxide; this of course removing the excess of free acid. The resulting brown liquid had still an acid reaction, but when a large excess of zinc oxide was added it became colourless, and ultimately the whole of the vanadium was completely precipitated from solution.

This behaviour of a solution of the trioxide with zinc oxide indicates that the green solution is an acid salt, whilst the brown is probably basic, a conclusion supported, moreover, by the fact that a few drops of acid turned the brown liquid green again.

I endeavoured to isolate a pure solution of the trioxide by reducing a pure solution of V_2O_5 in dilute sulphuric acid with metallic zinc, until the deep green colour of the trioxide was produced. This green solution, filtered and mixed with alcohol, deposited an intensely green oily liquid which could be separated from the lighter watery portion by means of a funnel. I found, however, that it was impossible to separate the vanadium salt from the zinc sulphate by long continued washing with alcohol, or by any other means tried. I then endeavoured to obtain by electrolysis a solution of V_2O_3 in sulphuric acid uncontaminated with any foreign substance. This method was

found to answer satisfactorily, the apparatus being arranged so that all the hydrogen was utilised and the oxygen carried away without interfering with the reduction. Fig. 1 shows the arrangement adopted. The reduction is best commenced on a strong pure solution of V_2O_4 in dilute H_2SO_4, which is readily obtained by the reducing action of SO_2. The deep blue tetroxide solution is placed in the platinum dish (*b*) forming the negative electrode of the battery (*d*), whilst the porous cell (*a*) containing the positive electrode of pla-

FIG. 1.



tinum (*c*) and dilute sulphuric acid just touches the surface of the liquid. The reduction proceeds regularly and may be accelerated by heating. In this manner, the reduction and evaporation can go on simultaneously. The end of the reaction is determined by the intense green colour of the solution, a drop of which on being taken out and shaken up with a small quantity of water gives a green liquid with no tinge of blue.

The concentrated green trioxide solution is then mixed with about twice its bulk of strong sulphuric acid, and allowed to remain for 24 hours; at the end of that time the whole of the trioxide separates in combination with sulphuric acid as a pale green sandy crystalline precipitate, which must be placed upon a porous tile, washed with strong alcohol until the free sulphuric acid is entirely removed, and then dried over sulphuric acid in a desiccator filled with coal-gas. The following analyses made with two preparations show that this sulphate of vanadium trioxide has the formula $V_2O_3(SO_3)_4 + 9H_2O$:—

	Calculated.	Found.	Found.
V_2O_3	23·78	23·93	23·81
SO_3	50·60	50·89	50·82
H_2O	25·62	25·18	25·37
	100·00	100·00	100·00

The vanadium was estimated as V_2O_5 by heating the salt in a crucible to bright redness, a fine crystalline residue of V_2O_5 remaining. The degree of oxidation was confirmed by means of a standard solution of permanganate, 1 c.c. of which was equal to 0·000677 gram of oxygen; 0·1120 gram of salt required 7·9 c.c. = 0·0053483 oxygen. The oxygen required by theory being 0·00566. The variation which is equal to 1 per cent. is only very small when the readiness with which the salt absorbs oxygen is considered.

Sulphate of vanadium trioxide dissolves in water, yielding a bright green solution, from which alkalis precipitate the hydrated trioxide as a dirty green somewhat gelatinous mass, which is rapidly oxidised in the air.

The fact that the brown trioxide solution is more basic than the above was ascertained by the fact that this green hydrated trioxide readily dissolves in a solution of the foregoing green sulphate, forming a deep chocolate-coloured liquid, and on evaporation this liquid yields a shining green amorphous mass, which again dissolves in water, forming a brown solution.

This method of reduction may also be employed for the preparation of the other lower oxides of vanadium. Thus a lavender-coloured solution of vanadium dioxide is obtained on continued reduction, and from this the hydrated dioxide may be precipitated by ammonia as a deep purple gelatinous mass.

It is, however, impossible to isolate these compounds in the solid state on account of their extreme instability.

LXXIX.—*On Ammonia-derivatives of Benzoïn.*

By Francis R. Japp, F.R.S., and W. H. Wilson, Ph.D.

The action of alcoholic ammonia on benzoïn was studied by Laurent and later by J. Erdmann (*Annalen*, **135**, 181). Both these chemists obtained a substance of the formula $C_{28}H_{24}N_2O$, to which Laurent gave the name *benzoïnam*. Erdmann further isolated a substance which he called *benzoïnimide*, assigning to it the formula $C_{14}H_{11}N$. Lophine was also formed.

The results which one of us had obtained in revising the work of Laurent and others on the ammonia-derivatives of benzil, appeared to render it desirable to re-investigate the action of ammonia on benzoïn.

The following is the method employed by Erdmann in preparing the above compounds. Benzoïn was heated with an excess of alcoholic ammonia in sealed tubes at 100°, for four to six hours. During the heating, the liquid deposited silky needles of benzoïnam, which were afterwards separated by filtration. On allowing the mother-liquor to evaporate spontaneously, it yielded a yellow crystalline mass, which by treatment with boiling alcohol could be separated into two portions, an insoluble yellow crystalline powder (Erdmann's benzoïnimide, which was analysed in this condition, without further purification), and a soluble portion, containing lophine together with a granular substance, the latter being obtained in quantity insufficient for investigation.

We conducted the operation in the above manner and observed the separation of benzoïnam as described by Erdmann. According to Erdmann this compound is insoluble in alcohol: he therefore contented himself with boiling the product with alcohol and analysing the supposed insoluble residue. We find, however, that by boiling with a large volume of alcohol the substance dissolves; the solution may then be concentrated by distilling off the alcohol, without any separation of substance, and on standing, the concentrated solution deposits the benzoïnam in tufts of long silky colourless needles. This process of purification was repeated until a sample of the product, when treated with concentrated sulphuric acid, no longer gave a red coloration, thus denoting the absence of Erdmann's benzoïnimide. The melting point could not be determined, as the substance decomposed on heating, and melted at temperatures varying from 190° to 220° according as the temperature was raised slowly or rapidly.

Benzoïnam dissolves much more readily in boiling benzene than in alcohol. Laurent's statement that it is soluble in water is incorrect.

Analysis of a specimen dried at 120° confirmed the formula $C_{28}H_{24}N_2O$ given by Laurent and by Erdmann. We quote the figures, as Erdmann's analyses were made with benzoïnam which had not been purified by recrystallisation.

	Substance.	CO_2.	H_2O.
I	0·1882	0·5726	0·1026
II	0·1988	0·6040	0·1073

III. 0·1273 gram, burnt with copper oxide in a vacuum, gave 13·79 c.c. of a mixture of nitrogen and nitric oxide, measured dry at 12·8° and under 409·7 mm. pressure. After absorption of the nitric oxide, there remained 13·79 c.c. of dry nitrogen at 12·8° and under 396·2 mm. pressure.

	Calculated for $C_{28}H_{24}N_2O$.		Found.		
			I.	II.	III.
C_{28}	336	83·17	82·98	82·86	—
H_{24}........	24	5·94	6·06	6·00	—
N_2	28	6·93	—	—	6·89
O	16	3·96	—	—	—
	404	100·00			

The yellow mother-liquor from the tubes from which the benzoïnam had been separated was evaporated to a small bulk, allowed to crystallise, and the yellow crystalline substance removed by filtration. When, however, following Erdmann's directions, we attempted to separate this product, by boiling with alcohol, into a soluble and an insoluble portion, we found that by employing sufficient alcohol and boiling sufficiently long the whole dissolved. The solution thus obtained, when concentrated and allowed to stand, deposited two sorts of crystals—yellowish needles of Erdmann's benzoïnimide, which gave the characteristic blood-red colour with concentrated sulphuric acid, and granular crystals (Erdmann's granular substance), the latter separating much more slowly and adhering for the most part to the sides of the flask. A mechanical separation was effected by shaking the contents of the flask before pouring on to the filter, the needles remaining suspended in the liquid whilst the granular crystals at once sank. The latter were put on one side for subsequent examination.

The so-called benzoïnimide (we shall show later on that this term is a misnomer) is not, therefore, as Erdmann asserts, insoluble in alcohol, but only sparingly soluble; it is in fact considerably more soluble than

benzoïnam and may be readily recrystallised. Boiling amyl alcohol dissolves it still more easily, and deposits it on cooling. The best solvent, however, is boiling benzene, which dissolves it very readily, and deposits it in lustrous, flat, obliquely truncated needles.

Erdmann obtained the substance, as already mentioned, in the form of a *yellow* crystalline powder, and we found that this yellow colour could not be removed merely by recrystallisation from alcohol. The substance is, however, colourless when pure. The method which we employed in purifying it is again in contradiction to Erdmann's statements as to the solubility of the substance. According to Erdmann, it is insoluble in an alcoholic solution of hydrochloric acid. It is true that a dilute solution of gaseous hydrochloric acid in alcohol does not dissolve the substance appreciably more than pure alcohol, but saturated alcoholic hydrochloric acid dissolves it very readily in the cold,* and the substance may be precipitated from the solution in *colourless* needles by the addition of alcohol. One advantage of this method is that as benzoïnam, lophine, and benzoïnidam (*vide infra*)—the other substances formed in the benzoïn-ammonia reactions—are readily soluble in dilute alcoholic hydrochloric acid, they remain in the mother-liquor. The benzoïnimide thus purified was finally recrystallised from a large volume of boiling alcohol,† and was thus obtained in slender, very lustrous, flat needles, which melted at 246° (no melting point is given by Erdmann), sublimed at a higher temperature without decomposition, and gave the characteristic red coloration with concentrated sulphuric acid.

The analysis of the compound dried at 120° gave results agreeing better with the formula $C_{28}H_{20}N_2$ than with the formula $C_{14}H_{11}N$, assigned to it by Erdmann:—

	Substance.	CO_2.	H_2O.
I	0·1076	0·3439	0·0518
II	0·2328	0·7450	0·1123
III	0·2323	0·7429	0·1115

IV. 0·2220 gram, burnt with copper oxide in a vacuum, gave 22·63 c.c. of a mixture of nitrogen and nitric oxide, measured dry at 12·5° and under 464·6 mm. pressure. After absorption of the nitric oxide, there remained 22·63 c.c. of dry nitrogen at 12·5° and under 443·1 mm. pressure.

* The solution is yellow, and if very concentrated speedily deposits a yellow crystalline substance—probably an unstable hydrochloride—which by exposure to the air, or by contact with alcohol, becomes white, and is converted into the original compound.

† At the time this specimen was prepared, we were not aware that the substance was soluble in benzene.

	Calculated for $C_{28}H_{20}N_2$ (Japp & Wilson).	Calculated for $C_{14}H_{11}N$ (Erdmann).	Found. I.	II.	III.	IV.
C....	87·50	87·05	87·17	87·28	87·22	—
H...	5·21	5·70	5·35	5·36	5·33	—
N...	7·29	7·25	—	—	—	7·31
	100·00	100·00				

The percentage of carbon found is too high for Erdmann's formula, and that of hydrogen too low; and this applies also to Erdmann's own analysis, which gave C 87·31, and H 5·61 per cent. Erdmann was doubtless led to adopt the simpler formula by the ease with which it enabled him to explain the formation of the substance as a condensation of ammonia and benzoïn with elimination of water, whereas the formula to which we give the preference requires the simultaneous abstraction of hydrogen:—

$$\underset{\text{Benzoïn.}}{2C_{14}H_{12}O_2} + 2NH_3 = C_{28}H_{20}N_2 + 4H_2O + H_2.$$

The reaction corresponds with that in which diphenanthrylene-azotide is formed from phenanthraquinone and ammonia, except that in the latter case, as phenanthraquinone is an analogue of benzil and not of benzoïn, abstraction of oxygen occurs instead of abstraction of hydrogen:—

$$\underset{\text{Phenanthraquinone.}}{2C_{14}H_8O_2} + 2NH_3 = \underset{\text{Diphenanthrylene-azotide.}}{C_{28}H_{16}N_2} + 3H_2O + O.$$

Erdmann's compound has the same relation to benzil that diphenanthrylene-azotide has to phenanthraquinone:—

$C_{14}H_{10}O_2$ (Benzil).	$C_{14}H_8O_2$ (Phenanthraquinone).
$C_{28}H_{20}N_2$ (Erdmann's compound).	$C_{28}H_{16}N_2$ (Diphenanthrylene-azotide).

Following out this analogy, we propose to name Erdmann's compound *ditolane-azotide*. The name given to it by Erdmann—*benzoïn-imide*—is misleading: the compound cannot be an imide.

In ditolane-azotide, two tolane-groups are united by two nitrogen-atoms; in diphenanthrylene-azotide two phenanthrylene-groups are united by two nitrogen-atoms. The very great stability of these compounds renders it probable that the nitrogen-atoms form part of a closed-chain complex. Their constitution might therefore be expressed by the following formulæ—

$$\begin{array}{c} C_6H_5{\cdot}C{-}N{-}C{\cdot}C_6H_5 \\ \;\;\;\;\;\;\;\;\;| \;\;\;\;\;\;\;\; | \\ C_6H_5{\cdot}C{-}N{-}C{\cdot}C_6H_5 \end{array} \qquad \begin{array}{c} C_6H_4{\cdot}C{-}N{-}C{\cdot}C_6H_4 \\ | \;\;\;\;\; | \;\;\;\;\;\;\;\;\; | \;\;\; | \\ C_6H_4{\cdot}C{-}N{-}C{\cdot}C_6H_4 \end{array}$$

Ditolane-azotide. Diphenanthrylene-azotide.

in which the mode of distribution of the available affinities in the closed-chain complex is left undecided.

There are various points of resemblance in the character and behaviour of these two compounds. Both are substances of very sparing solubility (diphenanthrylene-azotide is practically insoluble in the ordinary organic solvents of low boiling point). Both have a high melting point. Both sublime at a high temperature in flat lustrous needles, and both give characteristic colour reactions with concentrated sulphuric acid—ditolane-azotide giving a splendid red colour, diphenanthrylene-azotide a deep blue. The more sparing solubility, the higher melting point, and the higher temperature of volatilisation, are, as usual, on the side of the diphenylene-derivative as compared with the diphenyl-derivative.

The fact that ditolane-azotide is the most stable of the ammonia-derivatives of benzoïn rendered it probable that the yield of this substance might be increased by allowing ammonia to act upon benzoïn at a higher temperature. We found that this result might be very readily and effectually attained, and the substance prepared in any desired quantity, by heating benzoïn with ammonium acetate. 100 grams of glacial acetic acid were heated in a flask over a free flame, adding solid ammonium carbonate until the acid was neutralised and ammoniacal vapours began to be given off. 100 grams of benzoïn were then added, and the heating was continued until the whole of the ammonium acetate had been driven off and the benzoïn-derivative began to volatilise. The flask must be shaken the whole time to prevent cracking. The melted product, without allowing it to cool, was poured in a thin stream into excess of alcohol, ground in a mortar with the alcohol, and after complete disintegration, extracted with boiling alcohol. The residue consisting of ditolane-azotide with a small quantity of lophine was dried, dissolved in the cold in saturated alcoholic hydrochloric acid, the solution poured into excess of boiling alcohol, and the whole digested over the water-bath for some time. Ditolane-azotide was precipitated in minute needles, whilst lophine and yellow impurities remained in solution. For analysis, the substance may be recrystallised from boiling benzene, but, as precipitated, it is practically pure. The yield is about half the weight of the benzoïn employed; the use of sealed tubes is dispensed with, enabling a much larger quantity to be manipulated in a single operation; and all the troublesome processes of separation involved in Erdmann's process are dispensed with.*

* Fusion with ammonium acetate in an open flask may be advantageously substituted for heating with alcoholic ammonia in sealed tubes in the preparation of *stable* compounds usually obtained by the latter process. Thus we find that benzil gives, by this method, a good yield of benzilam, together with some lophine; and

We attempted to reduce ditolane-azotide by heating it with hydriodic acid and amorphous phosphorus, but without success. At low temperatures it was not attacked; at temperatures above 200° the nitrogen was eliminated as ammonia.

The granular substance already referred to (p. 826) was finely powdered, and dissolved by long boiling with alcohol. The solution was then distilled down to a small volume and allowed to crystallise. The substance is again deposited very slowly in granular crystals. A few acicular crystals of ditolane-azotide are generally mixed with it at this stage; these are mechanically removed as already described (p. 826). The substance was recrystallised until it presented a perfectly homogeneous appearance. It consists of minute but well-defined oblique tables or prisms, and melts when pure at 199°. It gives no red coloration with concentrated sulphuric acid. It is somewhat more soluble in alcohol than ditolane-azotide.

We propose to name the compound *benzoïnidam*.

The analysis of benzoïnidam dried at 120° gave the following results:—

	Substance.	CO_2.	H_2O.
I	0·1139	0·3458	0·0623
II	0·1642	0·4978	0·0895

III. 0·1334 gram, burnt with copper oxide in a vacuum, gave 13·79 c.c. of a mixture of nitrogen and nitric oxide, measured dry at 18·8° and under 249·2 mm. pressure. After absorption of the nitric oxide, there remained 13·79 c.c. of dry nitrogen at 19° and under 246·2 mm. pressure.

IV. 0·3504 gram gave 22·63 c.c. dry nitrogen + nitric oxide at 15·5° and 394·2 mm. After absorption: 22·63 c.c. dry nitrogen at 15·7° and 391·1 mm.

V. 0·2666 gram gave 13·79 c.c. dry nitrogen + nitric oxide at 18·8° and 500·3 mm. After absorption: 13·79 c.c. dry nitrogen at 18·8° and 481·7 mm.

These figures do not enable us to decide with certainty as to the formula of this compound. The formula which agrees best perhaps with the experimental results is $C_{28}H_{23}NO_2$:—

Mr. H. H. Robinson, working in this laboratory about four years ago, ascertained that phenanthraquinone could in this way be converted in the course of a few minutes into compounds which Sommaruga obtained by heating it with alcoholic ammonia in sealed tubes for 36 hours. From the product of the reaction, Mr. Robinson isolated diphenanthrylene-azotide and diphenanthrylene-oxytriimide.

	Calculated for $C_{28}H_{23}NO_2$.		Found. I.	II.	III.	IV.	V.
C_{28}....	336	82·96	82·80	82·68	—	—	—
H_{23}...	23	5·68	6·08	6·06	—	—	—
N	14	3·46	—	—	3·96	3·97	3·93
O_2....	32	7·90	—	—	—	—	—
	405	100·00					

Different preparations were employed in the nitrogen determinations.

The formula $C_{28}H_{23}NO_2$ is recommended by its simple relation to that of benzoïnam, $C_{28}H_{24}N_2O$, the latter compound being a condensation-product of 2 mols. of benzoïn with 2 mols. of ammonia, whilst benzoïnidam would be formed from 2 mols. of benzoïn and 1 mol. of ammonia :—

$$\underset{\text{Benzoïn.}}{2C_{14}H_{12}O_2} + NH_3 = \underset{\text{Benzoïnidam.}}{C_{28}H_{23}NO_2} + 2H_2O.$$

On the other hand, it must be pointed out that the discrepancy between the calculated and the experimental values for nitrogen *considerably exceeds* the experimental error of the very exact method of determination employed (see Trans., 1886, 475).

We do not, therefore, regard the above formula of benzoïnidam as established.

The smallness of the yield of benzoïnidam renders a study of its decompositions, which would doubtless throw light upon its formula, a practical impossibility.

We found, however, that the best yield of the compound was obtained by allowing ammonia to act for some weeks upon benzoïn in the cold with exclusion of air. The benzoïnidam gradually separates in moderately large transparent crystals, which may be mechanically separated from the slender acicular crystals of the other products present, and purified as already described.

The last mother-liquors from the sealed tubes, after the removal of the yellow crystalline substance (see p. 826), yielded lophine, identified by its melting point, Erdmann's observations as to the formation of this compound being thus confirmed.

We have to thank Mr. Cosmo Innes Burton for the great care with which he has made the various analyses given in this paper.

Normal School of Science,
South Kensington.

LXXX.—*Note on a Compound from Benzil and Isopropyl Alcohol.*

By Francis R. Japp, F.R.S., and Julius Raschen.

In a former communication, it was shown (Japp and Owens, Trans., 1885, 90) that in presence of a small quantity of caustic potash, benzil and ethyl alcohol unite, with elimination of water, yielding a compound of the formula $C_{30}H_{24}O_4$. The reaction occurs according to the equation $2C_{14}H_{10}O_2 + C_2H_6O = C_{30}H_{24}O_4 + H_2O$.

We have now made experiments to ascertain whether benzil reacts in a similar manner with other alcohols; but only in the case of isopropyl alcohol did the alcohol take part in the reaction. With propyl alcohol and isobutyl alcohol, there appeared to be merely a rapid reaction occurring even in the cold, between the benzil and the potash, to form potassium benzilate.

In the case of isopropyl alcohol, the experiment was conducted in the following manner. The potash (2 grams) was dissolved in 100 c.c. of isopropyl alcohol contained in a flask, and to the solution 10 grams of finely powdered benzil were added, after which the flask was tightly corked to exclude air, and shaken as long as the benzil dissolved. After standing for some months, the liquid contained a quantity of a pulverulent substance in which large transparent yellow crystals were imbedded. The solid substance was separated by filtration and washed, first with ether, to remove unaltered benzil, and afterwards with water, to dissolve potassium benzilate. The residue was sparingly soluble in alcohol, but dissolved after long boiling and, on cooling, was deposited in very lustrous, transparent, faintly yellowish crystals, of rhombohedral habit. After another recrystallisation from boiling alcohol, the substance was almost colourless. The crystals contained no alcohol of crystallisation (differing in this respect from the ethyl compound), and melted, with previous softening, at 147—148°.

The analyses agreed with the formula $C_{31}H_{28}O_4$:—

	Substance.	CO_2.	H_2O.
I	0·1665	0·4883	0·0912
II	0·1505	0·4411	0·0822

	Calculated for $C_{31}H_{28}O_4$.		Found. I.	Found. II.
C_{31}	372	80·17	79·98	79·93
H_{28}	28	6·03	6·09	6·07
O_4	64	13·80	—	—
	464	100·00		

The benzil and isopropyl alcohol react according to the equation—

$$2C_{14}H_{10}O_2 + C_3H_8O = C_{31}H_{28}O_4 + O.$$

The compound is therefore formed by a process of reduction, and is not analogous to the ethyl compound, which, as above stated, is formed from ethyl alcohol and benzil merely by elimination of water.

It may be noted that the formula $C_{31}H_{28}O_4$ is homologous with $C_{30}H_{26}O_4$, the formula ascribed by Limpricht and Schwanert to the ethyl compound (*cf. loc. cit.*). We therefore repeated the analysis of the latter compound, but merely confirmed the formula $C_{30}H_{24}O_4$, assigned to it by Japp and Owens.

In giving an account of the above results before the Society (see Proc., No. 24, p. 204), we stated that we had also obtained a new condensation compound of ethyl alcohol with benzoïn, formed by the action of very dilute alcoholic potash upon benzoïn in the cold. We have since found that pure alcohol does not yield this compound, and that its formation was due to an impurity contained in the methylated spirit which we employed, instead of duty-paid alcohol, in the experiment in question. We therefore reserve an account of this compound until we have more fully ascertained the conditions of its formation.

Normal School of Science,
South Kensington.

LXXXI.—*On Phosphorus Tetroxide.*

By T. E. Thorpe, F.R.S., and A. E. Tutton, Associate of the Normal School of Science, South Kensington.

When phosphorus glows in air at ordinary temperatures, phosphoric oxide is the only oxide of phosphorus formed. At slightly higher temperatures (50—60°), small quantities of phosphorous oxide begin to make their appearance in addition (see Cowper and Lewes, Trans., 1884, 10), but it is only when the phosphorus is actually ignited that any considerable amount of the latter compound is produced. Blondlot (*Compt. rend.*, **66**, 351) has indeed affirmed that the primary product of the union of phosphorus and oxygen is phosphoric oxide, and that phosphorous oxide is only formed by the action of the phos-

phorus upon the higher oxide: $3P_2O_5 + 4P = 5P_2O_3$. At moderately high temperatures, and with a limited supply of air, there is formed also, in addition to the phosphorous oxide, a light red or orange substance, which is frequently mistaken for amorphous phosphorus: this substance is, however, a true oxide of perfectly definite composition expressed by the formula P_4O. Its nature was first indicated by Le Verrier (*Annalen*, **27**, 167), who prepared considerable quantities of it, and studied its reactions. Reinitzer and Goldschmidt (*Ber.*, **13**, 845) also obtained the same substance by the action of zinc upon phosphoryl trichloride at 100°.

If the fumes formed by burning phosphorus in a limited supply of dry air are aspirated through glass tubes heated by steam, the deposited oxides are found to be free from admixed phosphorus. The alleged spontaneous inflammability of phosphorous oxide is really caused by this admixed phosphorus, which is probably present in the condition of the white phosphorus described by Remsen and Keiser (*Amer. Chem. Journ.*, **4**, 459). The relative proportion of the phosphorous and phosphoric oxides so formed will, of course, vary with the amount of oxygen present and the manner in which the combustion is made. According to Pagels (*J. pr. Chem.*, **69**, 24) the proportion of the phosphorous oxide rarely exceeds a third of that of the phosphoric oxide. We have, however, succeeded in getting products in which, as analysis showed, the amount of the phosphorous oxide was nearly equal to that of the phosphoric oxide present.

According to Reinitzer (*Ber.*, **14**, 1884) the mixture of oxides, when treated with water (care being taken to avoid any great rise of temperature), forms a *yellow* solution of neutral reaction which coagulates when heated to 80°. Reinitzer states that this substance is of the nature of a colloïd, since its solution is incapable of passing through a moistened membrane. We have made various attempts to obtain this singular body, but without success. On shaking a quantity of the mixed products of the combustion of phosphorus with pounded ice, they are rapidly dissolved, *occasionally* with the formation of an apparently yellow liquid. This liquid, no matter whether yellow or colourless, has invariably a strongly acid reaction, and when yellow could be obtained colourless by repeated filtration. On the filter, a very small quantity of a light orange extremely finely divided powder was obtained, which with alkalis and acids gave the reactions of Le Verrier's suboxide of phosphorus. The acid solution remained perfectly clear when heated to 80° with acids, and at once reduced silver nitrate and mercuric chloride.

A quantity of the mixed oxides obtained by the slow burning of phosphorus in air dried by oil of vitriol and phosphoric oxide was

transferred to a tube previously filled with dry carbon dioxide. After the introduction of the solid oxides, the end of the tube was drawn out and attached to a Sprengel pump, care being taken in all the operations to prevent the entrance of moisture.

The tube was carefully exhausted and sealed, and exposed at gradually increasing temperatures in baths of salts of known melting points. At about 290°, the white mass in the tube appeared to change; a considerable quantity of the orange or red suboxide was observed to form, and at some distance beyond was a sublimate of clear transparent and highly lustrous crystals. The coloured residue was subsequently found to be a mixture of phosphoric oxide and phosphorus suboxide. The crystals could be heated to 100° without the slightest change; at this temperature, the edges remained perfectly sharp, and no trace of fusion could be perceived. Hence they were not phosphorus. On heating to about 180° in a sulphuric acid bath, they volatilised and again formed just above the level of the liquid in the bath. The sublimate appeared to be perfectly homogeneous in character; it was made up partly of detached crystals and partly of aggregates showing precisely the same planes as the separate crystals. At the first glance the crystals seemed to be cubical in habitus, but on nearer examination the adjacent faces were found not to form right angles. Thin crystals gave very marked polarisation. In a considerable number of the crystals, the edges were modified, and on rotating under crossed Nicols the maxima of extinction were found to occur when the modifying edge was parallel with the plane of vibration of either Nicol, or whenever a crystallographic axis coincided with a plane of polarisation. The polarisation characters preclude the possibility of their being tetragonal, and their whole symmetry indicates that they are not hexagonal. Mr. L. Fletcher, of the Mineralogical Department of the British Museum, who was good enough to examine a number of specimens for us, confirms our opinion that the substance is almost certainly orthorhombic. No crystallographic measurements are possible in contact with air, as the crystals are so extremely deliquescent that they seem to liquefy after a few minutes' exposure in an open tube. They are almost instantly dissolved by water with considerable development of heat, forming a strongly acid solution, unchanged by boiling. With silver nitrate, the solution gives a white precipitate which rapidly blackens. It also reduces mercuric chloride to calomel on warming. Potassium permanganate solution is, however, only very slowly decolorised by it, even on warming after the addition of a few drops of sulphuric acid.

With "magnesia mixture" it gives an immediate precipitate of the double phosphate of magnesia and ammonia. After standing for

some time, the filtered liquid containing excess of gnesium chloride gave an abundant precipitate of phosphomolybd acid when treated with nitric acid and ammonium molybdate solution.

These tests are sufficient to show that the solution contained both phosphorous and phosphoric acids.

On concentrating the solution in a vacuum over oil of vitriol, it forms a colourless viscid syrup, consisting of a mixture of phosphorous and phosphoric acids.

On carefully neutralising a moderately concentrated solution of the mixed acids with soda, *no precipitation or formation of a sparingly soluble salt was observed* (*vide infra*). The neutralised solution placed in a vacuum over oil of vitriol yielded a thick syrup, which after long standing formed a crystalline mass. This behaviour is characteristic of solutions of *neutral* sodium phosphite.

The aqueous solution of the soda salts gave the following reactions:—

With silver nitrate, a yellow precipitate, changing to brown, and eventually becoming black. On boiling another portion of the solution with excess of soda, and again testing with silver nitrate, the same reaction was observed. Phosphites are not decomposed by boiling with alkalis, whereas hypophosphites are decomposed into a phosphate with elimination of hydrogen.

"Magnesia mixture" gave an immediate precipitate of magnesium ammonium phosphate. Phosphites and metaphosphates form no precipitate with magnesia salts in presence of ammonia, unless in very concentrated solutions. The saline mass consisted therefore of a mixture of sodium phosphite and orthophosphate. In order to determine the composition of the sublimed crystals, weighed quantities of them were allowed to deliquesce in air, the solution was diluted with water and evaporated with nitric acid.

Repeated evaporation with nitric acid is necessary in order to completely oxidise the phosphorous acid. Indeed it is only when the solution becomes concentrated and the nitric acid is strong that any oxidation can be perceived. The syrupy liquid from which the greater part of the nitric acid was expelled by evaporation was diluted with water and transferred to a platinum crucible containing a known weight of lime, which before the addition of the phosphoric acid solution was partially slaked by placing it for about 48 hours in an atmosphere saturated with water-vapour. The crucible and its contents were placed on the water-bath and afterwards cautiously heated to redness until the weight was constant. Preliminary experiments showed that a weighed quantity of lime after partial conversion into the nitrate can be obtained of the original weight by ignition. The validity of this method of determining phosphoric acid in an aqueous or nitric acid solution, which has certain

advantages over the usual process with litharge, was tested by estimations of the amount of phosphorus in phosphorus trichloride and in purified amorphous phosphorus. In both cases, numbers were obtained which were almost identical with those demanded by theory. Of course care must be taken when weighing the caustic lime that it does not absorb atmospheric moisture. The simple arrangement which one of us employed in weighing the hygroscopic titanic oxide in the course of a series of determinations of the atomic weight of titanium may be used in weighing the lime (Trans., 1885, 125). The crucible and its contents are placed under a cover made by inverting a light beaker with ground edges on a thin piece of sheet-glass; between the plate and the beaker is a narrow circular strip of thin sheet caoutchouc against which the beaker is pressed by an india-rubber band. The cover thus made fits air-tight, and the lime may be allowed to remain for hours without any increase of weight being perceived. In order to guard against any change of weight from the oxidation of the rubber or from its hygroscopic nature, the cover is weighed immediately after the determination of the weight of the lime.

Two determinations of the amount of phosphorus in the sublimed crystals afforded the following results:—

I	0·5300	gram gave	0·5961 P_2O_5.
II	0·3195	,,	0·3620 ,,

I	49·09	per cent. P.
II	49·46	,,
Calculated for P_2O_4	49·20	,,

P_2O_3 requires 56·36, and P_2O_5 43·66 per cent. P.

These numbers serve to indicate that the new oxide may be regarded as phosphorus tetroxide or hypophosphoric oxide, corresponding to the tetroxides of nitrogen and antimony. It is possible indeed that it is isomorphous with the latter compound, as cervantite, the native form of antimony tetroxide, is also orthorhombic. Whether, however, the molecular weight of this compound is expressed by the formula P_2O_4 remains to be proved. Although, as has been stated, the substance is volatile in a vacuum, we have not been able to obtain it in sufficient quantity to determine its vapour-density. A determination of vapour-density in a vacuum could not be readily carried out; the extreme rapidity with which the substance deliquesces would also add to the difficulty. The mode of its behaviour with water finds its simplest explanation on the assumption that the new oxide is phosphoroso-phosphoric oxide, P_2O_3,P_2O_5, exactly as the tetroxide of antimony is regarded as a compound of antimonious and antimonic oxides.

It may be assumed therefore to be the anhydride of the hypophosphoric acid or phosphoroso-phosphoric acid discovered by Salzer in the acid liquid obtained by partially immersing ordinary phosphorus in water in free contact with air (*Annalen*, **187**, 322). The constitution of this acid cannot as yet be said to be satisfactorily determined, but from the general character of its salts, a number of which have been prepared by Salzer and crystallographically examined by Haushofer and W. Fresenius, it is most probably represented as $P_4O_{12}H_8$ or $P_4O_4(OH)_8$.

Freshly prepared phosphoroso-phosphoric acid in moderately dilute aqueous solution does not, however, comport itself like a mixture of phosphorous and phosphoric acids. It can be boiled without change, and exerts no reducing action on solutions of the chlorides of mercury, gold, or platinum, and with silver nitrate it gives a white precipitate which is not blackened by boiling. Solution of potassium permanganate is quickly decolorised by it, especially on warming, whereas potassium permanganate is but very slowly reduced by phosphorous acid solution. With sodium carbonate or acetate, it gives a sparingly soluble acid sodium salt, probably $P_2O_6Na_2H_2,6H_2O$; none of these reactions are given by the solution obtained by the action of water upon the new oxide. We are disposed therefore to believe that it is not the anhydride of Salzer's acid, but that it is the true phosphorus tetroxide, P_2O_4, and that in the mode of its decomposition with water it behaves like nitrogen tetroxide at low temperatures:

$$N_2O_4 + H_2O = HNO_3 + HNO_2$$
$$P_2O_4 + 3H_2O = H_3PO_4 + H_3PO_3.$$

That it is not a mere combination of P_2O_5 and P_2O_3 seems to be further indicated by the invariable and simultaneous formation in relatively considerable quantities of the red suboxide. The loose light powder of the mixed combustion products of the phosphorus was almost perfectly white before being heated in a vacuum, but after heating the residue was invariably strongly coloured orange or light red. That it was the suboxide which was thus formed and not amorphous phosphorus was established by direct analysis. As the residue consisted mainly of phosphoric oxide and the red oxide, the tetroxide would seem to be derived from phosphorous oxide, possibly in accordance with the equation—

$$7P_2O_3 = 5P_2O_4 + P_4O.$$

The fact that a crystalline sublimate can be obtained by heating the combustion products of phosphorus has already been noticed by Hautefeuille and Perrey (*Compt. rend.*, **99**, 33), who, however,

describe the substance as one of the three modifications of phosphoric oxide, which according to them exist. No analytical data are given, but from the description of the mode of formation of the compound, its crystalline characters, and the different manner in which it is deposited according to the conditions of the sublimation, it seems not improbable that it is identical with the substance described in this communication.

LXXXII.—*A Chemical Study of Vegetable Albinism.* Part III. *Experiments with* Quercus rubra.

By A. H. Church, Professor of Chemistry to the Royal Academy of Arts.

In two former papers (this Journal, 1879, **35**, 33—41; 1880, **37**, 1—6) I described some conspicuous chemical differences between the white and the green foliage of seven distinct plants. These differences were shown in the constituents of the ash, in the nature of the calcium-compounds present, in the proportion of albuminoïd to total nitrogen, and in the relations of the living foliage to water and to the atmospheric carbon dioxide. With reference to most of these points, I am now able to add corroborative data drawn from the examination of the foliage of a forest tree. Mr. Nicholson, now Curator of the Royal Gardens at Kew, pointed out to me some time ago the existence of a very large albino bough on a fine and old specimen of the scarlet oak (*Quercus rubra*) of the Eastern United States. This bough is covered annually with white leaves, barely touched, here and there, with a few small isolated blotches of green. As is the case with albino foliage generally, these white oak-leaves are invariably smaller and thinner than the green leaves of the same age on the other boughs of the tree. The bough too itself is of less diameter and length (and so are its branches and twigs) than the green boughs of the same tree with which it may fairly be compared, the annual rings being narrower. There is a difference also in the colour of the bark of the albino bough, for it is a reddish-brown instead of a purplish-black.

Water, Organic Matter, and Ash.—On the 17th of August, 1880, a portion of the above-named albino oak bough was sawn off at the same time as a contiguous green bough; both were growing at a height of about 20 feet from the ground. The two specimens were at once taken to the Jodrell Laboratory and submitted to chemical

examination. The two kinds of leaves, after having been separated from their stems (but retaining their petioles), were analysed with all the precautions named in my previous papers. They gave the following results, calculated into percentages:—

	White.	Green.
Water	72·69	58·08
Organic matter........	24·65	40·33
Ash..................	2·66	1·59

The contrasts between the white and green leaves shown by these figures are in entire accordance with those observed in the case of the plants previously described, and are even more striking. For example, the difference in the percentages of water here amounts to no less than 14·61, whilst in my former trials it was as small as 4·88 in one case, that of *Plectogyne variegata*, and did not, in any instance, exceed 12·75 (in ivy). Then, again, the ratio between the organic matter and the ash in the fresh oak-leaves is most characteristic, the ratio being 100 to 10·8 in the case of the albino foliage, and 100 to 3·9 in the green; the difference between these ratios is larger than any previously observed.

Composition of the Ash.—We may now approach the consideration of the ash-constituents of these oak-leaves. On account of the abundance of material, I have been able to make a more complete examination of this mineral matter than was possible in the case of the plants before analysed. Potash, lime, magnesia, iron, phosphoric acid, and silica were the constituents to which my attention was previously confined; determinations of manganese, sulphuric acid, and chlorine have now been added. It may at once be stated that, of the three last-named constituents, the chlorine alone seems to be decidedly more characteristic of the albino than of the normal foliage. But this preponderance of chlorine in the white leaves can scarcely be due to any special function which it performs in them, but must be considered to result rather from the much greater quantity of potassium which accompanies it and from the easy diffusibility of the chloride.

The oak-leaves used in the fuller series of ash analyses were gathered on the 30th of July, 1886. It had been found that the first supply, picked on the 17th August, 1880, was not sufficient for all the determinations required. Still the following percentages selected from the experiments made with the 1880 crop may be here given:—

	White.	Green.
Ash in leaves dried at 100° C.	9·73	3·79
Potash (K_2O) in this ash	51·28	25·62
Phosphorus pentoxide in this ash....	14·64	17·05

It will be seen presently that these numbers agree well, so far as they go, with those obtained with the leaves gathered on the 30th July, 1886. The determinations were made in duplicate, and the following figures are the mean percentages:—

	White.	Green.
Ash in dry leaves of *Quercus rubra* ..	8·33	3·85
100 parts of this ash contained:—		
Potash (K_2O)	49·38	29·10
Lime (CaO)	8·25	24·50
Magnesia (MgO)	6·52	9·55
Ferric oxide (Fe_2O_3)................	0·82	1·24
Manganoso-manganic oxide (Mn_3O_4) ..	2·08	2·36
Phosphorus pentoxide (P_2O_5)........	14·25	15·80
Sulphur trioxide (SO_3)	7·18	10·05
Chlorine	4·25	1·25
Silica	3·15	4·25
	95·88	98·10
Deduct oxygen for chlorine	0·96	0·32
	94·92	97·78
Carbon dioxide, soda, &c., by difference	5·08	2·22

The above results do little more than confirm the conclusions reached by means of my inquiries of 1877–79. They show the same preponderance of potash over lime in the albino foliage, which the earlier analyses had revealed, of mineral matter over organic, and also the same remarkable deficiency of lime. As I stated in 1878, so I may now repeat, and with increased emphasis, "if we determine the water, the organic substance, and the constituents of the ash, in each of the following cases, we shall be able to affirm generally, that white leaves are related to green pretty much as immature leaves are to mature, tubers to foliage, petals to green bracts, vegetable parasites to their hosts."

Nitrogen-compounds.—The condition, or rather combination, in which the nitrogen exists in the white leaves as compared with its state in the green was determined in 1878 in one plant only, *Elæagnus pungens.* The same question has now been studied in the case of the scarlet oak: the results of the two sets of experiments are in satisfactory accord. In both plants, the total nitrogen and the non-albuminoïd nitrogen are higher in the white foliage than in the green; whilst the content of albuminoïd nitrogen is practically the same in both sorts of leaves, or at least in the dry matter of both sorts. I reproduce, from my first paper, the *Elæagnus* results,

placing them side by side with the corresponding figures of the oak; all the numbers represent percentages in the leaves dried at 100°.

	Elæagnus pungens.		*Quercus rubra.*	
	White.	Green.	White.	Green.
Total nitrogen	4·23	2·82	3·94	2·78
Albuminoïd nitrogen........	1·83	1·81	2·65	2·41
Non-albuminoïd nitrogen....	2·40	1·01	1·29	0·37

Thus in the two kinds of white leaves the percentage of albuminoïd nitrogen, as compared with the total, is 43 and 67; in the two kinds of green leaves, 64 and 87. The exact forms of combination in which the non-albuminoïd nitrogen exists in the albino foliage remain to be ascertained, but there can be no doubt that the excessive quantity of this nitrogen therein present is to be counted amongst the other signs of imperfect elaboration which analysis reveals. It should be stated that the above determinations of albuminoïd nitrogen were made by the phenol method.

Ether Extract, &c.—I purpose investigating the nature of the substances extracted by means of absolute ether from the albino oak foliage: here it must suffice to say that those extractives amounted to 5·35 and 5·15 parts respectively, from 100 of the dry white and green leaves. It is remarkable that, notwithstanding the absence of chlorophyll, the dry matter of the white leaves should yield a rather larger percentage of ether extract than that of the green; and this result becomes still more accentuated if we recall the fact that 100 parts of the dry white leaves contained less *total* organic matter (91·67 per cent.) than the green (96·15 per cent.). The nature of the organic substances, other than nitrogen-compounds, and of the matters soluble in dry ether, also demands investigation. I may, however, here state that a hot water extract of the white oak-leaves showed, with iodine solution, the reaction, not of starch, but of erythrodextrin, while both white and green leaves contained tannin.

Respiration and Transpiration.—The relation of the albino oak foliage to carbon dioxide and the atmosphere has been the subject of a few experiments, the final result of which may be thus expressed:—1000 square centimetres of surface of these albino leaves (counting one side only) produced in three hours 7·293 c.c. of carbon dioxide measured at 0° C. and 760 mm. bar. This figure corresponds with the elimination of 0·1097 gram of carbon dioxide per 100 grams of fresh albino leaves. The experiment was made on the 17th August, 1880; during two of the three hours of exposure the sun was shining. The operation was conducted in the way described in my memoir of 1879, but with this difference, that the whole volume of the air in

contact with the leaves was submitted to analysis. In a similar and simultaneous experiment with the normal green foliage, the whole of the carbon dioxide naturally present in the same bulk of air in contact with the leaves was withdrawn by the same area of leaf; probably the limits of this absorption were by no means reached.

Some experiments on the aqueous transpiration of the white foliage, as compared with that of the green, were made on the 17th August, 1880; the results were in but partial accord with those obtained with holly sprays in 1879 as recorded in my previous paper. Those, however, were obtained on a dull day, whilst during these more recent experiments with oak foliage the sun was shining during two hours out of three. A number of sprays of pure white oak foliage, 24·5 grams in weight, placed in separate vessels of distilled water, gained 0·46 gram during the three hours of exposure; whilst 19·5 grams of the green sprays lost, under the same conditions, 1·37 grams. When no water was supplied to the sprays, both the white and the green foliage lost considerably in weight and very nearly to the same extent. Further inquiry is needed before any definite conclusions can be drawn from these results, since, in the previous experiments with holly, the white sprays not supplied with water lost 6·54 per cent. of their weight, and the green sprays 10·26 per cent., during 3¼ hours' exposure. When water was supplied, the white holly sprays gained 0·29 per cent., and the green holly sprays, instead of losing weight like the green oak foliage, gained 1·55 per cent.

It remains to be added that the average weights of white and green oak-leaves, selected so as to be comparable, and deduced from 20 specimens of each sort, were:—

White	0·557 gram
Green	0·864 „

LXXXIII.—*Conversion of Ditolane-azotide into Diphenanthrylene-azotide.*

By FRANCIS R. JAPP, F.R.S., and COSMO INNES BURTON, B.Sc.

IN a recently published paper on the ammonia-derivatives of benzoïn, it was shown by one of us, in conjunction with Dr. W. H. Wilson, that the compound to which J. Erdmann assigned the formula $C_{14}H_{11}N$ (*Annalen*, **135**, 185) has in reality the formula $C_{28}H_{20}N_2$. It was further proposed to change the name of this compound from *benzoïnimide*—the name given by Erdmann—into *ditolane-azotide*, in

order to indicate its analogy to *diphenanthrylene-azotide*, $C_{28}H_{16}N_2$. The view taken as to the relation of these two compounds to one another was expressed in the following words (p. 828):—

"In ditolane-azotide two tolane-groups are united by two nitrogen-atoms; in diphenanthrylene-azotide two phenanthrylene-groups are united by two nitrogen-atoms. The very great stability of these compounds renders it probable that the nitrogen-atoms form part of a closed-chain complex. The constitution of the compounds might, therefore, be expressed by the following formulæ:—

$$\begin{array}{ccc} \begin{array}{l} C_6H_5{\cdot}C{-}N{-}C{\cdot}C_6H_5 \\ \qquad\;\;| \qquad\quad | \\ C_6H_5{\cdot}C{-}N{-}C{\cdot}C_6H_5 \end{array} & \qquad & \begin{array}{l} C_6H_4{\cdot}C{-}N{-}C{\cdot}C_6H_4 \\ \quad | \qquad | \qquad\quad | \quad\; | \\ C_6H_4{\cdot}C{-}N{-}C{\cdot}C_6H_4 \end{array} \\ \text{Ditolane-azotide.} & & \text{Diphenanthrylene-azotide.*} \end{array}$$

in which the mode of distribution of the available affinities in the closed-chain complex is left undecided."

In the above formulæ, ditolane-azotide is represented as containing four phenyl-groups, diphenanthrylene-azotide as containing two diphenylene-groups. Now Graebe has shown that compounds containing two phenyl-groups may frequently be converted, with elimination of hydrogen, into the corresponding diphenylene-compounds by passing them in a state of vapour through a red-hot tube: for example, stilbene, when thus treated, yields phenanthrene; diphenylamine yields carbazole. It seemed, therefore, possible that in this way ditolane-azotide might be converted into diphenanthrylene-azotide, a reaction which would exactly correspond with Graebe's synthesis of phenanthrene from stilbene. Such a transformation would go far towards proving the correctness of the assumption made in the paper just referred to, as to the analogy of ditolane-azotide to diphenanthrylene-azotide.

We, therefore, distilled a quantity of ditolane-azotide through a red-hot tube filled with fragments of glass; but from the tarry distillate nothing definite, beyond unchanged ditolane-azotide, could be obtained.

On again reading Erdmann's paper, however, we found an observation which appeared to point to an actual transformation of ditolane-azotide into diphenanthrylene-azotide. Erdmann mentions that in heating the former compound with soda-lime, he obtained a yellow, crystalline sublimate "which, by its behaviour towards concentrated sulphuric acid, showed itself to be a mixture of at least two compounds. One portion of the crystals dissolved in this acid with a

* Sommaruga, who first gave a name to this compound, calls it *diphenanthrene-azotide*, which is very much as if ethylene dichloride were to be termed *ethane-dichloride*.

magnificent deep-blue colour, another portion with a beautiful violet-red colour" (*Annalen*, **135**, 185). This deep-blue colour with concentrated sulphuric acid appeared to us to indicate the presence of diphenanthrylene-azotide, of which *this is the most characteristic* reaction; whilst the violet-red colour would be due to a mixture of this compound with unchanged ditolane-azotide, the latter compound yielding with sulphuric acid a blood-red colour, which, when mixed with the blue from the diphenanthrylene-azotide, might be expected to give a violet.

In order to test the correctness of this assumption, we mixed 5 grams of ditolane-azotide with powdered soda-lime and distilled it from combustion tubing over granulated soda-lime heated to medium redness. This time there was no tar formed; but a sublimate of flat yellow needles collected *close to the red-hot portion of the tube*—a behaviour highly characteristic of diphenanthrylene-azotide. Further along the tube, where the temperature was somewhat lower, a pale-yellow sublimate collected; whilst in a test-tube placed over the open end of the combustion tube the sublimate was white. The yellow needles gave, with concentrated sulphuric acid, an almost pure blue colour; the pale-yellow sublimate gave a violet, in which, while dissolving, separate streaks of red and blue were visible; whereas the white sublimate gave a pure red colour, and consisted of unaltered ditolane-azotide. In order to remove ditolane-azotide, the product of the distillation was boiled with benzene, which dissolves this compound readily, whilst it only takes up traces of diphenanthrylene-azotide. The residue was then treated with a concentrated solution of hydrochloric acid in alcohol, which also dissolves ditolane-azotide, but not diphenanthrylene-azotide. This last treatment was further intended to remove any traces of lime that might have been mechanically carried over during the distillation. Finally, the undissolved portion was washed with boiling alcohol, and dried for analysis. Thus purified, it consisted of a yellow, glistening crystalline powder. The yield was about one-tenth of the weight of ditolane-azotide taken.

Before analysing the substance, various qualitative tests were applied, in which it was compared with diphenanthrylene-azotide obtained from phenanthraquinone. The identity of behaviour in the two substances was absolute. Heated between watch-glasses, both sublimed at a very high temperature, condensing in flat, iridescent, yellow needles, sometimes obliquely truncated, sometimes notched at the end as if by twinning. Both dissolved in sulphuric acid, giving deep-blue solutions, indistinguishable from each other in tint. On gradually diluting the solutions with water the colour changed in both cases to orange, and on further dilution a practically colourless, amorphous substance was precipitated. According to Sommaruga diphenanthry-

lene-azotide does not melt at the boiling point of sulphur. A portion of the substance prepared from ditolane-azotide, enclosed in a capillary tube and heated in sulphur vapour, showed no sign of fusion.

Analysis of the product gave figures agreeing with those required for diphenanthrylene-azotide, $C_{28}H_{16}N_2$:—

	Substance.	CO_2.	H_2O.
I	0·1729	0·5593	0·0720

II. 0·1370 gram, burnt with copper oxide in a vacuum, gave 13·79 c.c. of a mixture of nitrogen and nitric oxide, measured dry at 17·5° and under 502·7 mm. pressure. After absorption of the nitric oxide there remained 13·79 c.c. of dry nitrogen at 17·5° and under 460·2 mm. pressure.

	Calculated for $C_{28}H_{16}N_2$.		Found.	
			I.	II.
C_{28}.....	336	88·42	88·22	—
H_{16}	16	4·21	4·63	—
N_2......	28	7·37	—	7·53
	380	100·00		

There is no doubt, therefore, that the compound obtained by the distillation of ditolane-azotide with soda-lime is diphenanthrylene-azotide, and it thus appears that J. Erdmann unconsciously synthesised this complex phenanthrene-derivative in 1865—seven years before the discovery of phenanthrene itself.

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LXXXIV.—*Action of the Halogens on the Salts of Organic Bases.* Part II. *Tetramethylammonium Salts.*

By Leonard Dobbin, Ph.D., University of Edinburgh, and Orme Masson, M.A., D.Sc., Professor of Chemistry in the University of Melbourne.

In a previous paper (Trans., 1885, 56), we detailed the results of experiments on the action of the halogens on the salts of trimethylsulphine. In that paper we showed that by acting with the halogens on the haloïd trimethylsulphine salts (Me_3SX), a series of addition products could be obtained, of the general formula Me_3SX_3, the

various members of which differed very much amongst themselves in their chemical and physical properties. Only in the cases where the products contained iodine, were we able to get crystalline substances fit for analysis; and those containing more than one atom of iodine in their molecules were either dark crystals which rapidly lost iodine when exposed to the air, or merely formed a dark tarry mass of polyiodide, from which a crystalline product could not be separated. Those products which did not contain iodine, but only bromine or chlorine or both, appeared as orange-red or yellow, more or less viscous liquids which decomposed slowly in dry air, losing halogen; or more rapidly in contact with water, trimethylsulphine salts remaining behind.

Although the peculiar character of some of these substances did not allow of their composition being accurately determined, it was shown that it might be expressed by the general formula Me_3SX_3 ($X = I$, Br, or Cl), and that all the compounds suggested by this formula may be obtained synthetically.

The property of taking up iodine, bromine, or chlorine to form addition products is by no means confined to the salts of trimethylsulphine, but seems to be common to the salts of many organic bases. We find that the reactions take place in the case of the salts of the nitrogen and of the phosphorus bases at least as readily as (and with those of the phosphorus bases perhaps more readily than) with the trimethylsulphine salts. It is the addition products obtained from the tetramethylammonium salts that we wish to describe in the present paper.

I. *Action of Iodine on Tetramethylammonium Iodide.*

This action has been described by Weltzien (*Annalen*, **99**, 1), who employed an alcoholic solution of iodine, and a solution of the iodide in aqueous alcohol, and obtained what he says was a pentiodide, or a mixture of this with triiodide, according to the proportion of iodine added. He describes these two compounds at considerable length, and mentions many of their chemical properties, but he does not give any analytical data except one iodine estimation in the triiodide.

II. *Action of Iodine on Tetramethylammonium Bromide and Chloride.*

On shaking up the dry solids with iodine dissolved in alcohol, solutions were obtained which, on evaporation in a vacuum, yielded small slightly-coloured crystals. The crystals from the bromide were orange, only slightly deliquescent in air, and rapidly lost iodine, leaving bromide. The crystals from the chloride were pale-yellow,

and also lost iodine rapidly, leaving behind a very deliquescent residue of chloride.

III. *Action of Bromine on Tetramethylammonium Iodide.*

The crystals of the iodide are turned brown directly they come in contact with bromine-vapour. When liquid bromine touches the dry iodide, a hissing sound is heard and much heat is developed. In the preparation of the addition product, bromine was added until there appeared to be no further action. The product is a dark pasty mass, which, in a current of air, loses the excess of bromine and becomes a hard solid of a colour much resembling that of cinnabar. This solid is reduced to powder, washed with ether, and dissolved in hot absolute alcohol, in which it is fairly soluble. On cooling, the alcoholic solution deposits feathery crystals of a deep orange colour. The mother-liquor, on evaporation, gives a crop of considerably larger crystals, mixed with colourless, slightly deliquescent crystals of a substance which proved to be tetramethylammonium bromide.

The portion of the substance used for analysis was part of the crop of crystals deposited from hot alcohol, and was dried for about 14 days over strong sulphuric acid.

The numbers obtained by analysis prove the substance to be tetramethylammonium dibromiodide, Me_4NI,Br_2, and are as follow :—

I. 0·3243 gram gave 0·1597 gram CO_2 and 0·1075 gram H_2O.
II. 0·3114 „ 0·1529 „ „ 0·1016 „

	Calculated.	Found. I.	Found. II.
C	13·29	13·43	13·39
H	3·32	3·68	3·62

A nitrogen determination was not made in this case, but the nitrogen was estimated in the analogous dichloriodide, to be described further on.

Tetramethylammonium dibromiodide crystals are quite stable, and not deliquescent even in moist air; they are almost insoluble in and seem to be scarcely decomposed by water. They are sparingly soluble in cold absolute alcohol, but moderately soluble in hot, and from the hot solution an abundant crop of crystals is deposited on cooling. They melt at 190° with very little apparent decomposition, their decomposition with evolution of iodine-vapour taking place at a considerably higher temperature. Treated with ammonia solution, they behave very like the corresponding trimethylsulphine compound, forming a dark, almost black substance which explodes on drying.

Action of Gaseous Ammonia on Tetramethylammonium Dibromiodide.

Having observed that trimethylsulphine dibromiodide united with dry ammonia to form a definite compound, $Me_3SIBr_2,2NH_3$, we tried the action of gaseous ammonia on the tetramethylammonium compound, and found that here also an analogous substance was formed. There was no apparent change in the orange crystals at first, nor until the ammonia had been passed for about an hour, when it was noticed that the orange colour had changed to a paler yellowish colour. Later, the substance became almost colourless, but minute yellow or orange particles could still be distinguished when constant weight had been reached.

0·3616 gram dibromiodide became 0·3960 gram by absorbing dry ammonia.

	Gain per cent.
Calculated for $Me_4NIBr_2,2NH_3$..............	9·41
Found	9·51

On exposing the product to the air for some days, the ammonia was given off again pretty rapidly, and the original orange colour of the dibromiodide was quite restored.

IV. *Action of Chlorine on Tetramethylammonium Iodide.*

A quantity of the finely powdered iodide was placed in a small flask, and a current of dry chlorine passed over it. The powder, which at first became dark, very soon afterwards assumed a pale-yellowish colour, and then no further change appeared to take place. As the action was manifestly not finished, the heat of a steam-bath was applied, and after a few minutes there was a violent reaction. In certain patches the powder became black and semi-fluid. A species of ebullition, accompanied by the formation in considerable quantity of whitish fumes took place, extending outwards from these patches, and eventually spreading throughout the greater part of the substance. As the wave of ebullition passed outwards, the substance resolidified at each centre into a hard black solid, which, by the further action of chlorine, became light-yellow in colour to a certain extent, but complete conversion of the whole into a homogeneous yellow substance did not take place until the mass had been reduced to powder, and this had again been heated in the current of chlorine for about half an hour. The yellow powder obtained was dissolved, like the bromine compound, in hot alcohol, and the solution, on cooling, yielded yellow feathery crystals which were washed with alcohol and dried over strong sulphuric acid. The mother-liquor on evaporation also yielded some slightly larger crystals.

Analysis gave the following results, which agree with the composition Me_4NICl_2 :—

I. 0·3042 gram gave 0·1930 gram CO_2 and 0·1234 gram H_2O.
II. 0·3170 „ 0·2047 „ „ 0·1302 „

III. 0·2785 gram was ignited with soda-lime, and the products of combustion were passed through dilute hydrochloric acid. With platinic chloride, this acid gave a precipitate containing 0·0971 gram platinum.

	Calculated.	Found. I.	II.	III.
C............	17·64	17·30	17·61	—
H	4·41	4·50	4·56	—
N	5·15	—	—	4·95

Tetramethylammonium dichloriodide, like the dibromiodide, is quite stable in air, but is more easily decomposed on heating, and the alcoholic solution appears to undergo a good deal of change on long keeping, or when heated for some time. The crystals do not melt until a temperature of 216° to 220° is reached, and not without partial decomposition. A deep brown liquid is formed, and a slight yellowish distillate.

Ammonia solution acts on the dichloriodide as it does on the dibromiodide, forming a black explosive substance, possibly iodide of nitrogen.

Dry ammonia did not act on the dichloriodide nearly so readily, nor to such an extent as on the dibromiodide. As soon as it came in contact with the gas, the dichloriodide at once turned a rather dark olive-green colour, which very soon became lighter and continued to get lighter for a considerable time. After half an hour, the whole had assumed a greyish-green colour which did not undergo further change. The least trace of moisture caused this substance to turn superficially a colour exactly resembling cocoa. The absorption of ammonia was very slow from the beginning, and after three and a half hours (when it had all but ceased) the percentage gained was only 7·4, whereas the formula $Me_4NICl_2,2NH_3$ requires a percentage gain of 12·5. This reaction proving so sluggish, it was not further investigated.

A compound was obtained by Weltzien (*Annalen*, **99**, 11) by the recrystallisation from water of Me_4NICl_3, which had the composition of tetramethylammonium dichloriodide, and seems to be identical with it, although the analytical results given do not agree very closely with theory. He obtained the substance Me_4NICl_3 by passing

chlorine in excess into a solution of tetramethylammonium iodide, and evaporating the liquid produced.

Tilden (this Journal, 1866, 145) obtained tetrethylammonium dichloriodide by the action of protochloride of iodine on a hydrochloric acid solution of tetrethylammonium chloride. This substance appears to have properties resembling those of the corresponding methyl compound.

In one of his original papers describing the properties of tetrethylammonium compounds, Hofmann mentions halogen compounds which probably resembled those obtained by us from tetramethylammonium salts, although he thought them to be substitution compounds. He says (*Roy. Soc. Trans.*, 1851, 370) :—"The action of various chemical agents upon the compounds of tetrethylammonium gives rise to a series of very remarkable substances. Chlorine, bromine, and iodine convert the base into substitution products, in which the basic character of the original atom has disappeared; of these the bromine compound is distinguished by its splendid appearance, crystallising as it does from alcohol, in long, magnificent orange-yellow needles. The iodine compound too is very beautiful; it forms either on addition of iodine solution to the base, or on evaporating a solution of the iodide exposed to the action of the air. In fact, it is difficult to avoid the formation of this substance in recrystallising iodide of tetrethylammonium."

Although a future contribution detailing the properties of these bodies is promised, we have not been able to find their description in any subsequent papers.

V. *Action of Iodine Monochloride on Tetramethylammonium Bromide.*

This action very much resembles that of bromine on the iodide, in the phenomena displayed, the liquid chloride producing a hissing sound when poured on to the dried and powdered bromide. The resulting solid was well washed with ether, and recrystallised from hot alcohol. The recrystallised substance very much resembled in colour the dichloriodide, and analysis proved it to be this, contrary to our expectations, as we had fully expected to get the chlorbromiodide, $Me_4NIBrCl$.

0·3358 gram gave on combustion 0·2152 gram CO_2 and 0·1532 gram H_2O.

	Calculated for Me_4NICl_2.	Found.	Calculated for $Me_4NIBrCl$.
C	17·64	17·48	15·1
H........	4·41	5·07	3·8

From this analysis it would appear that in the case of tetramethyl-

ammonium bromide (unlike that of trimethylsulphine bromide), the bromine is displaced by another halogen (presumably chlorine) when acted on by iodine monochloride.

VI. *Action of Bromine on Tetramethylammonium Bromide and Chloride.*

The dry solids were both rapidly turned orange-brown by bromine-vapour. Both slowly became semi-liquid, and then solidified again somewhat on the surface. After this stage no further change was observable. On passing dry air for some time over the products, both became semi-liquid again, giving off bromine rapidly, and the dark-brown liquids, on continuing to pass air, partially resolidified. The semi-solid substances were treated with ether, when they immediately solidified. The solids were washed repeatedly with ether, then dissolved in alcohol and evaporated in a vacuum, when yellowish crystals were obtained in each case. These compounds were both very unstable, losing bromine quickly on exposure to moist air, and becoming colourless. The colourless chloride residue deliquesced very rapidly, and that from the bromide less rapidly. The crystals of both addition products were darkened by ammonia solution, and the dark substances produced dissolved afterwards in the ammonia solution with evolution of small bubbles of gas—probably nitrogen.

VII. *Action of Chlorine on Tetramethylammonium Bromide and Chloride.*

The dry solids when placed in a current of dry chlorine, were only slowly affected by it, and very little change of colour was noticeable. Both became slightly yellow in colour, but no tendency to become liquid was observed. After the gas had been passed for a considerable time, the products were examined. Both gave off a little chlorine in the air, but not at all abundantly. Moistened with water, no formation of bubbles of gas was observable in the case of the bromide, but there was a distinct darkening of colour, as if a displacement of bromine by chlorine only took place in presence of water. In the case of the chloride there was a slight evolution of chlorine. Both products, when exposed to moist air, quickly deliquesced—that obtained from the bromide far more rapidly than the almost non-deliquescent bromide itself would have done, showing that it had been converted by the chlorine in part at least into the very deliquescent chloride.

The rate of absorption of chlorine by the chloride was very slow, as the following quantitative experiment shows :—

Weight of substance taken.	Time in chlorine.	Increase of weight.	Increase per cent.
0·5942	$1\frac{1}{4}$ hours	0·0928	15·6
—	$2\frac{1}{2}$,,	0·1058	17·8

The calculated percentage increase for Me_4NCl_3 is 64·8.

VIII. *Action of Bromine on Tetramethylammonium Sulphate.*

The sulphate, dried for many hours at 100° in a current of dry air, was placed in a current of air charged with bromine-vapour. It was at once coloured brown, and took up bromine very rapidly, but did not become liquid except to a slight extent.

A quantitative experiment was made in this case, of which the details are given below:—

Weight of substance taken.	Time in bromine-vapour.	Increase of weight.	Increase per cent.
0·3364 gram	$2\frac{1}{4}$ hours	0·7134 gram	212
	$3\frac{1}{2}$,,	0·7194 ,,	213
	Time over solid caustic potash.	Increase reduced to:	Increase per cent.
	1 day	0·3286 gram	97·6
	3 days	0·2909 ,,	80·6
	17 ,,	0·2867 ,,	80·4

The percentage increase for Br_2 (calculated for $[Me_4N]_2SO_4,Br_2$) is 73·7, so the result of our experiment cannot be said to give much definite information. The sulphate, in an atmosphere of bromine, is capable of taking it up in large quantity, and the product, in dry air, loses a large proportion of this bromine again with great rapidity, to a certain point, when further loss practically ceases.

IX. *Action of Chlorine on Tetramethylammonium Sulphate.*

The perfectly dry colourless sulphate soon became pale-yellow in a current of chlorine, but it did not become liquid, nor was any further change visible after the first 10 minutes or so. The product placed in air rapidly deliquesced, giving off a little chlorine. Mixed with water, it dissolved very rapidly, small bubbles of chlorine being given off for some time.

Before leaving the experimental portion of this paper, we wish to mention an experiment made with tetrethylphosphonium iodide, which was the only suitable phosphonium compound at our immediate disposal.

X. *Action of Bromine on Tetrethylphosphonium Iodide.*

Bromine acts at once on the dry solid, turning it reddish-brown, and, after a time, a dark brown liquid is formed from the melting of the product. This liquid crystallises when the excess of bromine goes off, needle-like crystals shooting from the edges towards the centre. The solid thus formed dissolves pretty readily in and crystallises from cold alcohol. The crystals were bright and shining, and of an orange-yellow colour. We have not in the meantime further examined them.

The close analogy between the tetramethylammonium-derivatives described in the foregoing section and the trimethylsulphine-derivatives described in our former paper (already referred to) is obvious; the method of formation being identical in the two cases, and the chemical and physical properties strikingly similar. Various facts already established by others have convinced us, moreover, that the salts of many other organic bases are capable of yielding analogous compounds with the halogens; and preliminary experiments of our own have shown that, as might be expected, the reaction is also applicable to salts of phosphorus bases.

In evidence of the former statement, we may mention the papers of several investigators.

In a paper on the "Polybromides of the Tetrammonium Bases," Marquart (*J. pr. Chem.*, **1**, 429) describes, with some detail, the formation and properties of tetrethylammonium tribromide. To prepare this substance, he simply mixed tetrethylammonium bromide with bromine-water. It was fairly stable, and the analytical results are moderately close to theory. He says, that in trying to prepare the corresponding methyl compound he found it to be decidedly less stable, being decomposed on recrystallisation, with formation of bromide as well as tribromide. An attempt to get a polychloride by acting with chlorine-water on the chloride failed, as of course it must fail, polychlorides being decomposed in presence of water.

Addition products have been obtained from pyridine by the action of halogens. Hofmann (*Ber.*, **12**, 984) describes dibromopyridine—a substance which crystallises in fine orange crystals. Ramsay (see *Watts' Dict.*, 3rd Supp., 1700) acted on picoline and its salts with bromine, &c., and obtained various analogous products.

Ostermayer has lately published several papers on the "Action of Iodine Monochloride on Alkaloïds," &c. (Abstr., 1885, 672; *Ber.*, **18**, 591 and 2298), to which we will only refer here.

M. Dittmar has also recently published a paper on the "Reaction between Iodine Monochloride and the Alkaloïds" (*Ber.*, **18**, 1612). In

it he makes two statements on which we wish to comment. He says (p. 1614) that all alkaloïds which react with iodine monochloride, producing the characteristic bright-yellow precipitates with the ammonia reaction, to be described farther on, contain one or more pyridine-groups; and the number of the halogen-groups added on, corresponds, in general, with the number of pyridine-groups contained in the particular vegetable base. The ammonia reaction which he describes is the formation of a dark-green substance from the iodine monochloride compounds by the action of ammonia solution.

Farther on (p. 1616), he says that this ammonia reaction gives a key to the constitution of the substance which yields it, and that it is an excellent reagent for the group of chlorine and iodine, this group alone giving it.

We have shown, both here and in our previous paper, that the formation of a yellow crystalline compound with iodine monochloride takes place with substances which do not contain any pyridine-group, and that the ammonia reaction takes place with substances which do not contain both chlorine and iodine, *e.g.*, tetramethylammonium and trimethylsulphine dibromiodides. The fallacy of the first of these statements has been pointed out already by Ostermayer (*Ber.*, **18**, 2299), who shows that a yellow precipitate, giving the ammonia reaction, can be readily obtained from concentrated solutions of caffeïne.

The reaction between the halogens and iodine monochloride, and organic bases and their salts, is a very general one, and applicable to nitrogen, sulphur, and phosphorus compounds alike; there is, moreover, little doubt but that similar addition products are formed in the case of all those bases, the radicles of which are sufficiently positive,* and which are not completely broken up by the action of the halogens.

The exact constitution of these addition products is a matter of some interest, and has a bearing on the vexed question of the existence or non-existence of molecular compounds as distinct from atomic compounds. Of the trihaloid derivatives of trimethylsulphine, which may be taken as representative of the whole class, some would undoubtedly, if their properties were studied apart from those of the rest, be classed as molecular compounds by the supporters of the theory of two distinct kinds of combination; whilst others would, with almost equal certainty, be considered as true atomic compounds, on account of their stability when heated, and their other properties. Of the series—Me_3SIBr_2, $Me_3SIBrCl$, Me_3SICl_2, Me_3SBr_3, Me_3SBr_2Cl, Me_3SBrCl_2, Me_3SCl_3, the higher members—those which contain an atom of iodine—are crystalline substances, which remain solid and unchanged at temperatures near 100°, and, when they do decompose,

* Compare the action of halogens on diethylenesulphide-methylsulphine iodide (Masson, Trans., 1886, 239).

do not show any tendency to split into their original components. In this respect they do not in the least resemble hydrated salts or other typical so-called molecular compounds.* The lower members, on the other hand, though formed in a precisely analogous manner, display a tendency—which becomes more and more marked as we descend in the series—to split again into free halogen and trimethylsulphine salt; and they do so, in fact, more or less rapidly at the ordinary temperature unless preserved in an atmosphere of halogen vapour.

We thus have a continuous series of substances, to whose members it would be absurd to attribute totally different constitutions, but which shows the atomic compound characters at one end and the molecular compound characters at the other. This fact appears to us to give some support to the position of those who deny the existence of two modes of combination, distinct in kind from each other.

Dr. Armstrong, in his address to the Chemistry Section of the British Association (see Reports, 1885), suggested that the so-called molecular compounds are, in reality, atomic compounds which owe their existence to the special attraction of negative atoms for negative atoms, and their capability of manifesting towards one another a certain "residual affinity" which they do not manifest towards positive atoms.

Whichever of the two possible atomic constitutions be attributed to the compounds we are treating of, it appears to us that they afford excellent examples of this accumulation of negative atoms, a process which would appear to be manifested in a still higher degree by the unstable, but definite, compounds which they themselves form with ammonia, *e.g.*, $Me_3SIBr_2,2NH_3$. In the one case, if the constitution be represented by the general formula $Me_3S{-}X{<}^{X}_{X}$, it is merely the halogen that is affected; in the other, $Me_3S{\lessgtr}\begin{smallmatrix}X\\X\\X\end{smallmatrix}$, it is the central negative atom (sulphur, nitrogen, or phosphorus, as the case may be) that manifests residual affinity towards the halogens. On the whole we incline towards the latter view, for, as we have already pointed out, the sulphates of trimethylsulphine and tetramethylammonium form unstable compounds with bromine and chlorine, which bear the closest resemblance to the corresponding trichlorides. A closer study of the phosphonium addition products than we have yet made may throw some further light on the question, for these should be more stable than the others (on account of the greater affinity of phosphorus for the halogens) if our view be correct.

* Compare on this point Kolbe (remark on Marquart's paper, *J. pr. Chem.*, 1, 435).

We have again to express our thanks to Professor Crum Brown for his advice and assistance during the progress of our work.

LXXXV.—*Glycyphyllin, the Sweet Principle of* Smilax glycyphylla.

By EDWARD H. RENNIE, M.A. (Sydney), D.Sc. (London), Professor of Chemistry in the University of Adelaide, South Australia.

IN a paper by Dr. C. R. Alder-Wright and the author which appeared in the Journal of this Society (Trans., 1881, 237), a partial description was given of a crystalline substance extracted from the leaves of *Smilax glycyphylla*,* a plant growing in abundance on the shores of Port Jackson, and common on the coasts of the northern parts of New South Wales and the southern parts of Queensland. The investigation was not completed from want of material, and although the writer obtained a grant from the Society some three years ago for a further examination of this substance, other duties have prevented, until quite recently, the completion of the work.

The results obtained confirm in some respects those published in the paper above referred to, but have shown that the formula therein proposed needs alteration. In brief, the substance has the formula $C_{21}H_{24}O_9 + 3H_2O$ when crystallised from aqueous ether, and $C_{21}H_{24}O_9 + 4\frac{1}{2}H_2O$ when crystallised from water. When boiled with dilute sulphuric acid, it undergoes decomposition in accordance with the equation—

$$C_{21}H_{24}O_9 + 2H_2O = C_{15}H_{14}O_5 + C_6H_{14}O_6,$$

forming *phloretin* and *isodulcite*, and is therefore closely allied to phlorizin. A discussion of these results will be found in the detailed account which follows.

Extraction and Purification.

In order to obtain the material for this investigation, about 75 lbs. weight of the leaves and stems were macerated for several days with strong spirit (till the leaves became tasteless) and the alcohol distilled off. The dark-coloured syrupy liquid was then exhausted with ether (a tedious process, as ether does not dissolve the substance very

* As the leaves treated were not submitted to an expert, it is possible that among them were some from *Smilax australis*, but the majority were from the above-mentioned species.

freely), and the ether distilled off. The residue always solidified on cooling to a dark-brown or yellow mass of crystals mixed with more or less semi-fluid resinous matter. The best method of effecting a rough purification was found to be solution and repeated crystallisation from hot water containing a *little* alcohol, rejecting any resinous matter which refused to dissolve easily. By this means, the greater part of the colouring matter could be removed and a mass of yellowish crystals was obtained, which, however, obstinately refused to become colourless by crystallisation alone. The further purification was effected by one of two methods.

1. The substance was dissolved in warm water, allowed to cool until just about to crystallise, then quickly shaken up with ether, and the latter rapidly poured off through a dry filter into a dry flask. On standing, a great part of the substance separated out as a perfectly white mass of minute crystals.

2. The substance was dissolved in hot water, some acetate of lead added, and the precipitate, which formed in larger or smaller quantity according as the solution was darker or lighter in colour, filtered through a hot-water filter and rejected. Sulphuretted hydrogen was then passed through the solution, the lead sulphide filtered off, the liquid being still warm enough to keep the substance in solution, and the filtrate allowed to crystallise. It was sometimes found necessary to repeat this process in order to get a perfectly white product, but it was finally adopted as the easier.

Composition and Properties.

The crystals deposited from a warm aqueous solution consisted of very brittle, slender four-sided prisms, often from one-half to one inch in length, if the solution had been slowly cooled. Whether separated from ether (under the conditions described above) or from water, they contain water of crystallisation, but not the same in amount (details given below). The following are the results of several combustions of different samples of anhydrous substance (dried at from 100—110°), Nos. I, II, III prepared by the ether process, and the remainder by the acetate of lead process :—

	Substance.	CO_2.	H_2O.
I	0·3535	0·7735	0·1980
II	0·2680	0·5865	0·1425
III	0·3073	0·6689	0·1640
IV	0·3390	0·7375	0·1825
V	0·3255	0·7100	0·1755
VI	0·3249	0·7085	0·1735
VII	0·2902	0·6352	0·1550
VIII	0·2474	0·5404	0·1314

	Calculated for $C_{21}H_{24}O_9$.		I.	II.	III.	IV.
C_{21}....	252	60·00	59·67	59·35	59·36	59·33
H_{24}....	24	5·70	6·22	5·83	5·93	5·98
O_9....	144	34·30	—	—	—	—
	420	100·00				

	V.	VI.	VII.	VIII.
C	59·49	59·47	59·69	59·57
H.....	5·99	5·93	5·93	5·90
O	—	—	—	—

The following table gives in percentages the results of several water determinations made in *different* samples, dried at 100—110°:—

						Mean.
Crystallised from ether	11·31	11·88	11·84	11·43	11·13	11·54
Crystallised from water	16·28	16·17	16·31	16·11	—	16·22

The formula $C_{21}H_{24}O_9 + 3H_2O$ requires 11·39 per cent. of water.
„ $C_{21}H_{24}O_9 + 4\frac{1}{2}H_2O$ „ 16·16 „ „

A combustion of an *air-dried* specimen (crystallised from water) gave carbon 49·85 per cent., hydrogen 6·55 per cent., theory requiring carbon 50·29 per cent., and hydrogen 6·58 per cent., thus confirming the above results.

For the present at least, I propose to retain for this substance the name *glycyphyllin*, suggested in the joint paper already quoted, as it appears to be quite different from the substance described under the name of *smilacin* and from other known substances. It has no well-defined melting point, but at temperatures varying from about 110° to 115° it begins to show signs of change, and as the temperature rises, is gradually transformed into a caramel-like substance, which at 175—180° melts with decomposition. It is only very sparingly soluble in cold water, but sufficiently so to communicate to the solution its characteristic strong liquorice-like taste. It is easily soluble in hot water and alcohol, soluble to some extent in ether, insoluble in chloroform, benzene, and light petroleum. It dissolves in solutions of the caustic alkalis, and the solution gradually assumes a rich reddish-brown colour on exposure to the air. It does not reduce Fehling's solution. Its solution is not precipitated by ordinary acetate of lead, but is immediately precipitated by the basic acetate.

It was not possible in this case to get an accurate estimate of the yield of material, but it could not have been more than one-half, and was probably nearer one-third per cent.

Decomposition by Dilute Sulphuric Acid.

When an aqueous solution of glycyphyllin is boiled in a flask with reversed condenser, with the addition of a small quantity of dilute sulphuric acid, the liquid soon becomes turbid, and rapidly deposits an almost colourless crystalline powder. On cooling, a small quantity more separates out, the liquid having at the same time acquired the power of reducing Fehling's solution. As the precipitated substance is never obtained quite white, it is purified by dissolving it in a hot mixture of alcohol and water (about equal volumes), adding acetate of lead, filtering off any slight precipitate, passing sulphuretted hydrogen, &c., &c. The filtrate, on cooling, deposits a snow-white crystalline mass, which is anhydrous. The following are the analytical numbers obtained from different samples:—

	Substance.	CO_2.	H_2O.
I	0·2030	0·4857	0·1015
II	0·2690	0·6486	0·1295
III	0·2885	0·6962	0·1370
IV	0·2558	0·6170	0·1220
V	0·2535	0·6063	0·1225
VI	0·2532	0·6064	0·1244

	Calculated for $C_{15}H_{14}O_5$.		I.	II.	III.	IV.	V.	VI.
C_{15} ..	180	65·69	65·25	65·76*	65·82*	65·78*	65·22	65·31
H_{14} ..	14	5·11	5·52	5·35	5·28	5·29	5·36	5·45
O_5 ..	80	29·20	—	—	—	—	—	—
	274	100·00						

These numbers agree satisfactorily with those required by the formula $C_{15}H_{14}O_5$, which is ascribed to *phloretin*, and, on further examination, leaves no doubt as to the identity of the two substances. The substance obtained as described above is almost insoluble in cold water, and only very sparingly soluble in boiling water, from which it crystallises on cooling in minute shining prisms. It is easily soluble in alcohol, and crystallises from a hot mixture of alcohol and water in groups of needles radiating from a centre. It is soluble also in ether and hot glacial acetic acid. It melts at 250° with decomposition. Stas gives the melting point of phloretin as 180°, and this at first misled me, but it has since been shown by Schiff (*Ber.*, **14**,

* In these combustions, the oxygen which had been used in the combustions was inadvertently allowed to remain in the tubes while weighing, thus accounting to some extent for a somewhat high percentage of carbon.

303) that the melting point is close to 250°. It dissolves with yellow coloration in solutions of the caustic alkalis and of the alkaline carbonates, and is reprecipitated on acidifying. The solution in strong ammonia, after a short time, deposits golden-yellow scales. When boiled with strong caustic potash for from 15 to 20 minutes, the solution is no longer precipitated on addition of an acid, and is found to contain *phloroglucol* and an acid which is to all appearance identical with *phloretic* acid.

To isolate these substances, the alkaline solution was first slightly acidified with hydrochloric acid, rendered slightly alkaline with sodium hydrogen carbonate, and then exhausted with ether. The residue after the evaporation of the ether was decolorised partly by the aid of animal charcoal and partly by the acetate of lead process, and then crystallised several times from water. The crystals contained water of crystallisation, and had a very sweet taste. The melting point of the anhydrous substance was found to be 208—209°.* The aqueous solution gave a deep reddish colour with ferric chloride. On combustion, the following numbers were obtained:—

	Substance.	CO_2.	H_2O lost.
I	0·2220	0·4627	—
II	0·3046	0·6328	0·1357

	Calculated for $C_6H_6O_3$.		I.	II.
C_6	72	57·14	56·84	56·66
H_6	6	4·76	—	4·95
O_3	48	38·10	—	—
	126	100·00		

There can be no doubt, therefore, that the substance in hand was *phloroglucol.*

The solution from which the phloroglucol had been removed was acidified by hydrochloric acid, and again exhausted with ether. On evaporation, a mass of dark-coloured prismatic crystals remained. These were decolorised by animal charcoal and several times recrystallised from hot water; by slow cooling, crystals were often obtained an inch in length. On combustion, the following numbers were obtained:—

	Substance.	CO_2.	H_2O.
I	0·2532	0·6000	0·1440

* This is the melting point given in all the more recent accounts of phloroglucol, although in *Miller's Chemistry* and elsewhere it is stated to be about 220°.

	Calculated for $C_9H_{10}O_3$.		I.
C_9	108	65·09	64·63
H_{10}	10	6·03	6·32
O_3	48	28·88	—
	166	100 00	

The silver salt was prepared by precipitating a solution of silver nitrate with a solution of the barium salt (obtained by boiling the acid with pure barium carbonate), washing the precipitate in a partially darkened room, drying it in the dark over sulphuric acid, and finally at 100°. It gave the following numbers on analysis:—

	Substance.	CO_2.	H_2O.	Ag.
I	0·3086	0·4494	0·0995	0·1212

	Calculated for $C_9H_9AgO_3$.		I.
C_9	108	39·56	39·72
H_9	9	3·58	3·29
Ag	108	39·56	39·27
O_3	48	17·30	—
	273	100·00	

The acid melted at 127—128°, and its aqueous solution gave a *slight* violet coloration with ferric chloride. In other physical characteristics, it agreed closely with the description given of phloretic acid, and it is obviously identical with the acid previously obtained by fusing glycyphyllin with caustic potash at 250°. Trinius, who has synthesised phloretic acid (*Annalen*, **227**, 262), states that when pure it gives no coloration with ferric chloride, but says that a sample prepared from phlorizin gave this coloration, and he concludes that the reaction is due to a small quantity of impurity in the acid, and that Rochleder's so-called isophloretic acid was really pure phloretic acid. The acid prepared as above described, even when repeatedly crystallised from water, converted into the silver salt, and regenerated from the latter, still gave the reaction. The colour produced, however, could hardly be said to be well marked, and is probably due, as Trinius suggests, to the presence of some impurity (phloroglucol?) which obstinately adheres to the acid prepared in this way. It may be remarked, however, that a single drop of ferric chloride solution, such as is usually employed as a reagent, gives scarcely a perceptible coloration, but the colour deepens considerably

on the addition of a further quantity. This may perhaps account to some extent for the discrepancy.

Examination of the Filtrate after Separation of the Phloretin.

The filtrate from the phloretin was neutralised by the addition of barium carbonate, the barium sulphate and excess of carbonate filtered off, and the solution evaporated to dryness. During this process, more or less of a red colouring matter was produced, but the syrup which remained soon crystallised. The crystals were washed once or twice with a little cold strong alcohol which removed most of the colouring matter, and then repeatedly crystallised from ordinary alcohol, but the product so obtained always had a slight molasses-like odour, and on combustion gave numbers which did not agree well with any probable formula. It was, therefore, recrystallised two or three times from very strong alcohol ($98\frac{1}{2}$ per cent.) until quite white and free from odour. Specimens so prepared melted at 93—94° when slowly heated in a capillary tube. It gave up one molecule of water on being heated at 100°. Three different samples gave the following results on analysis:—

	Substance.	CO_2.	H_2O.
I	0·2513	0·3657	0·1800
II	0·2495	0·3609	0·1785
III	0·2660	0·3828	0·1849

	Calculated for $C_6H_{14}O_6$.		I.	II.	III.
C_6	72	39·55	39·68	39·45	39·25
H_{14}	14	7·69	7·95	7·95	7·72
O_6	96	52·76	—	—	—
	182	100·00			

This substance was found to be sparingly soluble in cold alcohol, but easily soluble in the boiling liquid, from which, or from water by slow evaporation, it separated in well-formed monoclinic crystals agreeing exactly in appearance with the crystals of isodulcite obtained by Will from *naringin*, and figured by him (*Ber.*, **18**, 1318). It reduced Fehling's solution on boiling. The quantity obtained was insufficient to determine its specific rotatory power, but the above evidence is, I think, sufficient to identify it as isodulcite.

Quantitative Examination of the Decomposition by Dilute Sulphuric Acid.

In order to determine the equation representing the decomposition of glycyphyllin by dilute sulphuric acid, weighed quantities were boiled with suitable proportions of the dilute acid in a flask connected with a reflux condenser until the decomposition was judged to be complete. The liquid was allowed to cool, the phloretin filtered off, well washed with cold water, washed off the filter with alcohol, and the alcoholic solution evaporated to dryness. The filtrate and washings were then extracted with ether to remove small quantities of phloretin which still remained in solution, and the residue from the evaporation of the ether added to the main portion, the total product being finally dried at 100—110°. Four experiments of this kind were made with the following results:—

	Glycyphyllin (anhydrous).	Phloretin.	Per cent.
I	1·224	0·8055	65·63
II	11·479	7·463	65·01
III	5·239	3·474	66·31
IV	5·0033	3·317	66·30

In the last of these experiments, the liquid freed from phloretin was made up to 1 litre, and titrated with Fehling's solution. It was found that 26 c.c. were required to reduce 10 c.c. of Fehling's solution (1 c.c. = 0·005 glucose). Assuming that 10 c.c. Fehling's solution are reduced by 0·0549 gram isodulcite,* as recently determined by Will (*loc. cit.*), we have—

$$\text{total isodulcite} = \frac{1000 \times 0{\cdot}0549}{26} = 2{\cdot}115 \text{ grams.}$$

This is equal to 42·2 per cent. on the glycyphyllin taken. Considering the formation of small quantities of secondary products, such as colouring matter, these numbers agree as well as can be expected with those indicated by the equation—

$$C_{21}H_{24}O_9 + 2H_2O = C_{15}H_{14}O_5 + C_6H_{14}O_6,$$

which requires 65·22 per cent. of phloretin and 43·33 per cent. of isodulcite.

Discussion of above Results.

The formation of isodulcite by the decomposition of glycyphyllin

* In an actual experiment, a number very close to this was obtained for the reducing power of isodulcite, but the details and therefore the exact numbers were unfortunately lost.

is interesting as affording another instance of a so-called glucoside which yields isodulcite and not glucose on boiling with dilute acids. It has been shown that isodulcite has more than once been mistaken for glucose (*Ber.*, **15**, 215; **18**, 1316, *et seq.*). During the course of this investigation, it seemed possible that this might have happened in the examination of phlorizin, in which case glycyphyllin might be identical with that substance. The close resemblance in physical properties seemed to render this probable. Thus Schiff (*Ber.*, **14**, 303) states that phlorizin "melts at 110° to a semi-fluid opaque mass, which on further heating became again solid and porcelain-like, and at 170—171° melts to a clear yellow fluid;" this is very like the behaviour of glycyphyllin. Schiff also calls attention to Loewe's criticism on the results published with reference to phlorizin, especially as regards the discrepancies in the analytical numbers obtained.

On closer examination, however, the differences appear to be too great to be accounted for by any experimental error. The highest percentage of carbon obtained in the analysis of phlorizin is about 2 per cent. lower than that required for glycyphyllin; the amount of water of crystallisation found in phlorizin by several experimenters corresponds with only 2 mols. H_2O; and, finally, although Hesse states (*Miller's Organic Chemistry*, 5th edition, p. 582) that the sugar obtained from phlorizin is essentially different from glucose, yet he finds for its specific rotatory power in a solution freshly prepared $[\alpha]_D = 89$, a number more than 10 times as great as that given by several observers for isodulcite.

I have sent to Trommsdorf for a supply of phlorizin, in order to compare it with glycyphyllin, and if possible to ascertain the relationship between these two substances, and I hope, ere long, to communicate the results to the Society.

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ERRATA IN VOL. XLIX.

Page	Line		
7	7	from top,	*for* "15633" *read* "16233."
,,	8	,, ,,	,, "9138" ,, "9738."
,,	9	,, ,,	,, "(9138−9709 =) − 571" *read* "(9738−9709=)29."
,,	12 & 13	,, ,,	,, "2649" and "731" *read* "3249" and "1331."
,,	15—20	,, ,,	,, "none of them . . . . would do" *read* "the only one, the α-modification, which dissolves with the heat evolution with which the mixed salts would, is blue, whereas the mixture would be white, and that, of the two other modifications, one dissolves with an evolution of 3249 cal. less, and the other 1331 cal. more, than a simple mixture would."
15	14	,, ,,	,, "− 571" *read* "29."
481	18	,, ,,	,, "P_2S_5," ,, "P_2S_3."
535	6	,, ,,	,, "mercurosic," *read* "mercuric."
557	10	,, ,,	,, "mercury sulphite," *read* "mercurosic sulphite."
558	9	,, ,,	,, "Sartorious," *read* "Sartorius."
560	8	,, ,,	*for* "sulphate," *read* "sulphite."
572	15	from bottom,	*for* "sulphate," *read* "sulphite."
573	19	,, top,	*for* "sulphate," *read* "sulphite."
581	16	,, ,,	*for* "sulphate," *read* "sulphite."
563	17	,, ,,	*for* "no action," *read* "an action."
572	8	,, bottom,	*for* "sulphide," *read* "sulphite."
575	12	,, top,	*for* "$Hg<\begin{smallmatrix}O\cdot SO_2\cdot O\\ O\cdot SO_2\cdot O\end{smallmatrix}>Hg_2$," *read* "$Hg_2<\begin{smallmatrix}O\cdot SO_2\cdot O\\ O\cdot SO_2\cdot O\end{smallmatrix}>Hg_2$."
583	8	,, ,,	,, "make," *read* "makes."
583	24	,, ,,	,, "H_2SO_3," *read* "$2H_2SO_3$."
587	13	,, bottom,	*for* "$\begin{smallmatrix}AgO\\ Hg-\end{smallmatrix}>SO_2$," *read* "$\begin{smallmatrix}AgO\\ Ag-\end{smallmatrix}>SO_2$.
625	18	from bottom,	*for* "NH·Y·NR," *read* "NH_2·Y·NHR."
,,	16	,, ,,	,, "NH_2·Y·NR," ,, "NH_2·Y·NHR."
,,	14	,, ,,	,, "NR·Y·NR," ,, "NHR·Y·NHR," and ,, "X·NHR_2," ,, "X·NHR."
747	21	,, top	,, "although benzene," *read* "although azoxybenzene."
757	6	,, bottom	,, "13 c.c.," ,, "10 c.c."
710	17	,, top	,, "extracted," ,, "estimated."

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